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# **Final Research Report**

**For**

**Radiophotoluminescent and Tenebrescent Glasses**

**Navy Department**

**Bureau of Ships**

**Electronic Division**

**NObsr-57016**

**NE-051551**

**2.3**

**By N. J. Kreidl**

**Chemical Research Director**

**Bausch & Lomb Optical Co.**

FINAL RESEARCH REPORT  
FOR  
RADIOPHOTOLUMINESCENT AND TENEBRESCENT GLASSES

BAUSCH & LOMB OPTICAL CO.  
ROCHESTER 2, NEW YORK

NAVY DEPARTMENT BUREAU OF SHIPS ELECTRONICS DIVISION  
Nobsr-57016 NE-051551 2.3

Copy No.

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ABSTRACT

It is impossible to find a single and simple dosimeter which will cover more than a segment of the entire range that has practical interest, say from  $1 \times 10^{-3}$  to  $1 \times 10^9$  roentgen units (r). However, in the range of specific interest for military and civilian defense purposes, say from 10 to  $10^3$ r the simple use of a glass is promising and worth detailed study.

The most successful glass remains the radiophotoluminescent potassium-barium-aluminum metaphosphate glass containing 2-16% silver phosphate. developed by Weyl et.al. and Schulman et.al. (1,2) which was found to be fluorescent proportional to radiation of a wide spectrum of high energy in the dose range of  $10 - 10^4$ r. One section of the phase of this study reported here, extends the theoretical investigation previously reported into an experimental study of the function of this glass. (This glass was also investigated under Contract NObsr-57010, Bausch & Lomb and Contract NObsr-49257, Polaroid Corporation.) Its sensitivity was found to be greatly affected by melting time, melting temperature, melting atmosphere, impurities imparted from raw materials, crucibles, and by deliberate contamination. An increase of sensitivity by contamination was observed with a large series of elements, and was particularly effective in the case of titanium and cerium.

These increases in sensitivity are of the order of 25% in standardized instruments using filters, and would attain 100% if filters were designed to enhance specific luminescence maxima with due consideration of noise signal ratios. Iron strongly decreases sensitivity, and manganese contamination is the most

pronounced single factor producing high pre-exposure ("pre-dose") fluorescence.

The only limitation in the general usefulness of the radiophotoluminescent glass is the indirect character of indication caused by the need to subject the exposed glass to a source of ultraviolet radiation to read the dose in the form of secondary luminescence. For this reason some additional work was devoted to vitreous systems that might indicate gamma radiation doses directly by visual color changes.

This section of experimental work resulted in the discovery of a fluorine and silver containing phosphate glass that will indicate a minimum dose of 20r by instrument and 100r visually to a trained observer. However, this and other glasses are not now considered practical, as an untrained observer will not easily recognize these changes in glasses of the largest practical dimensions, and as the usefulness of such a device becomes rapidly questionable if the minimum dose detected is much above 50r.

Two other phases of study were (1) the development of a "standard" glass in which manganese centers simulate the intensity and spectral character of the radiophotoluminescence of the exposed dosimeter glass in a glass insensitive to radiation and (2) a limited amount of scouting experiments on thermoluminescence in glass.

While thermoluminescence requires the "indirect" method of reheating, and has the additional limitation of exhaustion under test, it will remain of specific interest in high sensitivity dosimetry as long as crystals are shown to have milliroentgen sensitivities.

1.

PART I

1.1

PURPOSE

The purpose of this investigation is to determine, in glasses, the causes of optical changes produced by x - or gamma radiation, to select and develop these compositions which combine optimum indication and integration of x or gamma radiation with desirable technological properties affecting their eventual manufacture, and to develop a glass which without radiation by x or gamma rays will fluoresce in a manner similar to the existing dosimeter glass. The Radiophotoluminescent glass developed by W. A. Weyl and J. H. Schulman et.al. (1,2) is also to be investigated under this Contract. Contracts NObsr-57010 (Bausch & Lomb) and NObsr-49257 (Polaroid Corporation) are concerned with the Engineering and Instrumentation phases of this glass respectively.

1.2 GENERAL FACTUAL DATA

1.2.1 Personnel working on this project

<u>Names of Personnel</u>	<u>Position</u>	<u>Hours</u>
N. J. Kreidl	Director of Research	644
T. G. Pett	Head, Glass Physics Section	447
G. Blair	Project Engineer	2447
W. Kirchgessner	Spectroscopist	69
N. Iannone	Metallurgist	8
E. Herko	Chemist	33
G. Brewster	Chemist	66
G. Smith	Chemist	40
R. Plunkett	Chemist	78
J. Mogenhan	Chemist	45
R. Redinger	Technician	6
C. Cialdella	Chemist	16
R. Guenther	Technician	40
L. Bartle	Technician	6
M. Vetter	Technician	11
E. Simms	Technician	4
W. VandeMark	Technician	21
G. Biel	Technician	151
H. Gore	Technician	18

1.2.2 Test Equipment

1.2.2.1 CP-95(XN-3)/PD, Serial No. 19, with calibration standards supplied by the Polaroid Corporation of Cambridge, Massachusetts, was used to obtain readings on the radio-photoluminescent glass. Some of the readings were also taken at Polaroid.



- 1.2.2.2 A Co<sup>60</sup> source was used for all exposures. This equipment was described Interim Report 24 February to 24 March 1952.
- 1.2.2.3 A small annealing oven fitted with a Pyrex Glass Door was used for evaluating glasses for the property of thermoluminescence.
- 1.2.2.4 A humidity chamber, controlling both relative humidity and temperature, was used for Persistence Testing.
- 1.2.2.5 An ice-box utilizing dry-ice and a thermostatically controlled blower-fan was used for storage testing.
- 1.2.2.6 A Hunter Color - Color Difference Meter was used in evaluating color changes in the field of Tenebrescence.(10)
- 1.2.2.7 A Hardy Recording Spectrophotometer was used in evaluating changes in the visible range of the spectrum in the field of Tenebrescence.
- 1.2.3 Test Procedure (For Data in Appendix I, II, III)
- 1.2.3.1 The glass was machined into squares of the following dimensions-
- .750" x .750" x .175"
- The finish on the glass was -
- 1 edge (designated as exit edge)                      No. 320 grit grind
- 2 faces and 3 edges (1 face designated
- as U.V.Face)    No. 120 grit grind
- 1.2.3.2 One Face and three edges (other than exit edge and U.V.Face) were painted with non-fluorescing black paint.
- 1.2.3.3 The finished squares of glass were then placed in CP-95 (XN-3)/PD Reader, and the predose readings taken.
- 1.2.3.4 The squares were then irradiated with 100r of Co<sup>60</sup> gamma rays.

- 1.2.3.5 The squares were again placed in Reader, after a minimum hold time of 4 hrs. after exposure, and the postdose readings taken.
- 1.2.4 Definition of Terms
- 1.2.4.1 Predose - This term applies to the ultraviolet luminescence of the radiophotoluminescent glass prior to x or gamma radiation exposure. (measured in "Roentgens" on the CP-95 (XN-3)/PD)
- 1.2.4.2 Postdose - This term applies to the ultraviolet luminescence of the radiophotoluminescent glass after x or gamma radiation exposure. (measured in "Roentgens" on the CP-95 (XN-3)/PD.)
- 1.2.4.3 Sensitivity - This term is the percent of true dose represented by actual indication. The readings are listed as deviations from unity. In other words, it is the postdose reading minus the predose reading, the difference divided by the true dose, measurements being made on the CP-95(XN-3)/PD.
- 1.2.4.4 Judd - This unit is defined as the least perceptible change in color that is commercially practical.
- 1.2.4.5 Radiophotoluminescent - This is the property of a substance to fluoresce as the result of previous high energy irradiation. The fluorescent centers formed are of a permanent nature. In the case of the radiophotoluminescent glass, the fluorescence is excited by near U. V. irradiation.
- 1.2.4.6 Tenebrescence - This term refers to the change of visual absorption in a substance as the result of high energy irradiation.

1.3 DETAIL FACTUAL DATA

1.3.1 Introduction

At the present stage of technical thinking, an ideal dosimeter will be the one which, on exposure to atomic radiation, will induce changes in properties that are easily detectable by eyes rather than instruments. Colorimetric changes which can be easily detected by comparing with a standard previously prepared, probably represent the simplest system. The range should extend from a few milli-r ( $10^{-3}$ r) to over tens or hundreds of mega-r (1 mega-r =  $10^6$ r). The low limit is useful for health monitoring in daily routine check in plants or laboratories, while the high limit finds its use in places such as food sterilization, etc. For military or civilian defense purposes, the high limit may be set at 600r. It is impossible to find a single, simple dosimeter which will cover a range, say from  $1 \times 10^{-3}$  to  $1 \times 10^9$ r. A series of dosimeters each to cover a segment of the range may be desirable. However, the change of the properties, be it colorimetric or otherwise, should vary linearly with the dosage of the exposure. The change which occurs should also be relatively permanent. Since dosimeters may be used in numbers in the order of hundreds of millions in the time of emergency, they should be cheap, and easily reproduced. Possibly a glass can fulfill these requirements as well as any other material. Powdered crystals of special dyes or other organic substances or inorganic materials imbedded in a plastic may

be also considered. Chemical solutions may be also used with limitations. Single inorganic crystals are not desirable on the consideration of cost and reproducibility. In reality, the situation is far from satisfactory. While it is not difficult to induce color changes in a glass, a solution, or a crystal, with a radiation dosage in the limits ( $10^2$ -  $10^3$ ) to  $10^8$ r, there is nothing as yet available that yield color changes for radiations lower than  $10^2$ r which are easily detectable by eye without the aid of instruments. In this lower region, one depends upon indirect methods for the measurement of dosages. The most successful one is that developed by W. A. Weyl and J. H. Schulman et. al. (1,2) who took advantage of the fact that the change produced by the radiations may be detected through its fluorescent nature. A phosphate glass containing 2-16 wt. % silver phosphate was found to be fluorescent after exposure to a radiation dosage in the limit of  $10$ - $10^4$ r. The silver ions were reduced to silver atoms through the action of radiation; the latter fluoresce upon irradiation with ultraviolet rays. For radiation dosages lower than 10r, other means are used. The well known photographic badges are popular, but they are inconvenient as they require photographic development. Single crystals of NaCl activated with 1% AgCl or some ZnS phosphor (Fonda phosphor) are known to emit light upon heating or irradiating with light after the exposure to radiations with intensity as low as a milli-r or lower (3,4). The phenomenon is called thermoluminescence. The extension of the study of thermoluminescence.

to glass has been emphasized in a previous report by Sun and Kreidl (5). Because of the practical significance of silver-containing radiophotoluminescent glass, despite its limitation in dosage limit, the present investigation is concerned largely with the further development of this type of dosimeter and with the development of a suitable standard glass necessary for calibrating the instrument used to measure the radiophotoluminescence of the glass. Some attention was also directed toward the study of direct colormetric dosimeters and the thermoluminescent effect. The investigation has been limited at first to glass for arbitrary demarcation. This should not be considered as the limit of thinking of the investigators. The details are described as follows:

1.3.2 Further Investigations on the Radiophotoluminescent Glass

The radiophotoluminescent glass developed by Weyl and Schulman et.al., as mentioned previously, is essentially a phosphate glass composed of meta-phosphates of Ag,K,Ba and Al. The range of application of this glass is about  $10^{-10}$  to  $10^4$  r. In order to control radiation specifications, and also because of the fact that the glass represents an entirely new type from the point of view of glass technology, an investigation was carried out to ascertain the reproducibility of the glass. It was soon found out during the investigation that small amounts of impurities such as  $TiO_2$  affect the radiation sensitivity of this dosimeter glass. Experiments of this nature have always been time consuming and tedious.

However, the effect was established at least qualitatively. A large number of glass melts were also made to study the effect of other variables such as the melting time, melting containers, melting temperature and compositions of the basic glass. All these are separately described in the following sections.

- 1.3.2.1 Melting Time: One of the main serious effects of melting time is the reduction of silver from ionic silver in glass to atomic silver. Since radiation reduces silver ions to atoms, and it is the fluorescent effect of the silver atoms that one detects, it is obvious that initially i.e. prior to irradiation, the glass should contain none of the free atoms or as few as possible. The length of melting time apparently has some effect on the reduction of silver ions and on initial fluorescence, termed the pre-dose level. Depending on particular raw materials used, a certain amount of time is necessary to incorporate the silver in ionic form into the glass. Prolonged melting causes the initial fluorescence level to increase indicating the reduction of silver ions. An optimum length of time is easily determined as long as one is aware of the effect of the prolonged heating.

- 1.3.2.2 Melting Temperatures: As was the case with melting time, there is an optimum melting temperature to give minimum initial fluorescence which also seems to impart the greatest sensitivity to the glass.
- 1.3.2.3 Melting Containers: A zircon crucible has been found to be very satisfactory for laboratory melting. Vycor and platinum crucibles are also usable without apparent contamination. A platinum-rhodium crucible did not prove to be satisfactory since the phosphate glass dissolved the rhodium from the crucible, giving the glass color and seriously affecting its properties. A clay crucible is usable; however, the glass does attack the clay to a slight degree dissolving out a small amount of iron which has a serious effect on the sensitivity.
- 1.3.2.4 Melting Atmospheres: Because of the fact that silver should be kept in ionic rather than atomic form in glass, the neutral or preferably slightly oxidizing atmosphere prevalent in an ordinary electric furnace is desirable.

All the experimental evidences relating the effect of melting time, temperature, container, etc. are summarized in table form in Appendix I.

- 1.3.2.5 Raw Materials: The variation of raw materials stands out as the greatest single factor affecting the properties of the glass. The purity of the raw materials as to their iron and manganese content give wide variations in initial fluorescence and sensitivity from one particular combination of raw materials to another. Iron was deliberately added to a repeat melt of known properties. A 0.02% by wt. addition of  $\text{Fe}_2\text{O}_3$  gave a two-thirds reduction in sensitivity. Additions of very small amounts of  $\text{MnO}_2$  (0.01%) greatly increase the initial fluorescence level (approx. 10 times). These are indicated in Appendix II.
- 1.3.2.6 Composition of the Base Glass: Although the original base glass was of the potassium-barium-aluminum-phosphate type, there is no reason why other phosphates may not be used. In addition, ionic silver is readily soluble in borate type glass and J. Schulman and collaborators (oral communication patents applied for) have demonstrated the



applicability of this type of glass for silver-containing dosimeters. Silicate type glasses are not desirable as pointed out by Weyl because of the limited solubility of silver in these glasses.

Because of the strict limitation in specifications, the present investigation covers only the limited variations of the original base glass of the phosphate type. A series of glasses were made by substituting Li, Na and Rb for the K in the original glass. The effect of the substitutions may be briefly summarized as follows:

(a) Li for K - This substitution yields higher radiation sensitivity (15% increase) as measured on standard instrument.

(b) Na for K - The resulting glasses gave a somewhat higher initial fluorescence level (approx. 10X) and the fluorescent band is shifted toward a shorter wavelength as observed visually. However, these glasses also show an increase in sensitivity of from 10-15% as measured on instrument.

(c) Rb for K - The substitution was not satisfactory because complete solution of the materials was not achieved. No mixed substitutions of (Li and K), (Li and Na) or other combinations for K were made.

#### 1.3.2.7 Effect of Small Amount of Foreign Materials:

This work resulted from the discovery that a very small addition of  $TiO_2$  to this glass causes a measurable increased fluorescence sensitivity, and incidentally, in-

creases the direct coloration sensitivity. This work has been expanded to include additions of over 30 elements (mostly as oxides) in various concentrations. Some of the elements which visibly show a fluorescence sensitizing action in concentrations of 0.001% and/or 0.01% by wt. are - Ti, Rb, Cs, Ce, Ge, V, Cr, Sn, Hf, Pb, Th, Co, Nd, Sb, As, Cd, Pt, Ir, Au, F, and I. Of these Cs, Ti, Ge, Ce, Pt, and Ir show the greatest increase in sensitivity which is, in some cases, as high as 40% as measured on an instrument similar to that described by Schulman et.al. (1). The instrument readings on the glasses containing sensitizers in addition to silver were probably low because the instrument is adjusted by filters to pass light corresponding to the maximum of the fluorescence spectrum of the base glass containing only silver whereas the glasses containing sensitizers in addition to silver had different maxima. Visually the fluorescence sensitivity seemed to be increased from 3 to 5 times. The work accomplished at this point also indicates another fact. The additions of larger concentrations of most of the ingredients studied show the effect of radiophotoluminescence quenching. Complete quenching was noticed when additions of over 0.01% -Ti, 0.1% - Ce, 0.01% - V, 0.1% - Cr, 0.1% - Co, 0.1% - Se, were added and smaller effects of quenching were noticed on larger additions of other elements. Other work on this particular phase has included additions of two or more sen-

sensitizing elements in one glass. This does not appear to sensitize to any greater degree than some one component addition to glasses made to-date. Samples were prepared and readings taken on some of the glasses made in this study. These are summarized in Appendix III. Although only preliminary and qualitative evidence has been obtained so far in this work, the results do indicate that an increase of fluorescence sensitivity of from 5 to 10 times the present level might be realized. The greater sensitivity in fluorescence brought about by these changes may prove to be valuable in the detection of smaller dosages than the present range of the silver phosphate "Dosimeter Glass".

Because of the importance of small impurities in glass, work on analytical determination of these trace materials has been carried out. By spectrographic determination the iron impurity level in a "target glass" (a glass having a mean sensitivity specified during this program) was found to be 0.005%. The details of the analytical work are given in Appendix IV.

1.3.2.8 Composition and Schedule of 8" Clay Pot Production Melt  
Melt No. E-9880 represents glass that has acceptable characteristics of initial fluorescence and sensitivity (Pre-dose-30r, Sensitivity - .80). The sensitivity can be varied by using different surface finishes on the two exposed surfaces of glass and by varying the thickness of the sample. These factors will give a variation

up to 25% that is easily controlled. The composition and schedule are as follows:

Composition

<u>Raw Material</u>	<u>Lot Designation</u>	<u>Wt. %</u>	<u>Batch Weight</u>
Al(PO <sub>3</sub> ) <sub>3</sub>	F	50	3500 gm.
Ba(PO <sub>3</sub> ) <sub>2</sub>	C	25	1750 gm.
KPO <sub>3</sub>	D	20	1400 gm.
KNO <sub>3</sub>	-	5	350 gm.
AgPO <sub>3</sub>	A	8	560 gm.

The materials are weighed out and screened through a 20 mesh screen. The material is then mixed with a plastic paddle in an aluminum-lined wooden box. Special precautions are taken in making up batch to avoid contamination (especially iron).

Schedule

Filling Temperature and Time - 1100°C - 1 hour

Melting Temperature and Time - 1120°C - Hold for 4 hrs

Stirring - Start as soon as fills are melted down and continue to stir until ready to cast.

Casting Temperature - 950°C - Cast as soon as furnace reaches this temperature.

Annealing - Anneal in continuous electric lehr. Temperature - 450°C.

NOTE: The melt was made in an 8" clay pot with a clay thimble stirrer in a Glo-Bar Furnace.

1.3.2.9 Effect of Heat Treatment on Exposed Glass

Experiments were carried out to see if the effect in the glass caused by gamma radiation could be erased by heat treatment, i.e. the chemical change resulting from photon bombardment was reversible. Machined squares of Melt E-9880 were painted and the predose readings

taken. The samples were then divided into two groups. One group was irradiated with 100r of Cobalt-60 gamma rays and postdose readings taken. The paint was removed from both groups and the samples were placed in an oven at 450°C (the annealing temperature of the glass) and held for 3 hours. The two groups of samples were then repainted and readings taken. The two groups read the same, however both had shifted upward 10 units from the original predose readings.

To explain this shift another experiment was carried out where one group of samples were not painted before heat treatment and the other group was painted, predose readings taken, and paint removed. The two groups were then placed in an oven at 450°C for 3 hours. The two groups were then painted and readings taken. The group containing samples unpainted before heat treatment gave readings similar to those on the other group before heat treatment, whereas the samples that had been painted before heat treatment again shifted up 10 units. This was true even after heat treatment for as long as 100 hours at 450°C, indicating that - the predose fluorescence of the glass is reasonably stable at this temperature; the paint was apparently not completely removed from the samples and caused an increase in fluorescence after heat treatment, and the chemical change in the glass resulting from photon bombardment is reversible when the glass is held at 450°C for at least 3 hours.

The samples of glass that had been exposed to 100r of Cobalt-60 gamma rays and then heat treated, were exposed again to 100r. On comparing the sensitivity of the glass after this exposure with the first exposure, it is evident that the radiophotoluminescent properties of the glass have remained the same.

1.3.2.10 Further Testing of the Radiophotoluminescent Glass

Additional testing was done on samples prepared from pressings of Melt Number E-9880. These tests were made to check conformance of the glass to Interim Military specification MIL-D-16153C (Ships). The tests were performed under the observation of personnel from the Sub-Office of Naval Inspector of Ordnance. The tests as specified in MIL-D-16153C (Ships) and the deviations from test conditions because of equipment limitations are as follows -

Par 3.6.1 Storage - The detector shall meet the requirements of this specification after having been stored at temperatures over the range from -55° to +85°C.

Par 3.6.2 Exposure Temperature - The detector shall be capable of detecting X and gamma radiation within the accuracy specified in 3.8.3 when exposed at 70° ± 10°F and over a temperature range from 20° to 140°F upon application of a linear temperature coefficient correction.

Deviation - Maximum temperature - range obtained was +55°F to +80°F.

Par 3.6.3 Reading Temperature - The detector shall be

capable of indicating dosage received within the accuracy specified in 3.8.3 when read 4 hours after exposure at a temperature of  $70^{\circ} \pm 5^{\circ}\text{F}$ , and over a temperature range of  $20^{\circ}\text{F}$  to  $140^{\circ}\text{F}$  upon application of a linear temperature - coefficient correction.

Par 3.8.2 Minimum Dose - The minimum detectable dose shall be no greater than 10 roentgens.

Par 3.8.3 Accuracy - The accuracy of the dosage indication over the entire range of detection shall meet the following: -

Par 3.8.3.1 The detector shall indicate the dose received within  $\pm 20\%$  of the true roentgen dose, or 10 roentgens, whichever is larger, when exposed to X or gamma radiation over the energy range from 80 thousand electron volts (80 Kev) to 1.5 million electron volts (1.5 Mev) for doses up to 600 roentgens. This radiation shall fall onto either face of the detector at normal incidence. The units shall be read in a CP-95(XN-3)/PD or CP-95( )/PD, calibrated to within  $\pm 2$  percent of mutually accepted standards. Over the energy range from 120 to 180 Kev, the detector shall indicate the dose received within  $\pm 40$  percent of the true roentgen dose, or 10 roentgens, whichever is larger.

Deviation - The samples were exposed to Co<sup>60</sup> radiation only, and were exposed in back of a 1mm lead plate instead of a lead shield as specified in par.3.4.2 for complete detector.

Par.3.8.3.2 Persistence - The intensity of the luminescent light emitted by the detector shall be persistent so that it shall be possible to read the indicated dosage repeatedly and still obtain readings of the accuracy specified in 3.8.3.1. It shall be possible to read the detector for a period up to 45 days after exposure and obtain the desired accuracy.

also:

Par. 4.3.6 Persistence test - Detectors which have been subjected to the operating tests of 4.3.2 shall be stored for a period of 45 days and then measured in a CP-95()/PD or CP-95(XN-3)/PD.

The measurements taken at the end of the 45 day period shall be compared with the measurements taken at the beginning to determine compliance with 3.8.3.2. In carrying out persistence tests, the effect of storing the DT-60 ( )/PD units in a range from -55° to / 60°C shall be determined. This may be accomplished by varying the temperature over



the temperature range during the 45 day test. Similarly, during this test the relative humidity shall be varied up to 95 percent.

Par.3.8.3.3 Additivity - The accuracy of any reading shall be the same whether the dose is received in a single continuous exposure or in several discrete exposures obtained at intervals varying from a few hours up to 45 days.

Par.3.8.3.4 Integration Rate - The detector shall be able to integrate radiation intensities up to the order of 10,000 roentgens per hour and still indicate dosage within the accuracy specified in 3.8.3.1.

Deviation - The maximum radiation intensity was approximately 25 roentgens per hour of Co<sup>60</sup>.

Par.3.8.3.5 Predose - The DT-60( )/PD shall have , prior to radiation exposure, an ultraviolet luminescence that shall be equivalent to the ultraviolet luminescence induced by 37~~7~~ roentgens.

The results of the testing are tabulated in Appendix V, and indicate that this glass meets the requirements of MIL-D-16153C to the limits tested.

1.3.3.0 Manganese Glass Used for Radiophotoluminescent Instrument Calibration

1.3.3.1 Development of Glass

In conjunction with the development of an instrument to measure the radiophotoluminescence of the silver phosph-

ate dosimeter glass, it was necessary to have a means of calibrating the instrument so that accurate readings could be obtained. For this purpose a manganese containing glass having similar fluorescence properties to a dosed silver phosphate glass was developed. Some of the requirements of this glass were that it have similar fluorescence color to a dosed silver phosphate glass, uniform u.v. absorption, good penetration by u.v. light, high transmission of orange light, stability of fluorescence under u.v. radiation, stability of fluorescence under gamma radiation, temperature coefficient of fluorescence similar to the silver phosphate glass, and intensity of fluorescent light similar to a silver phosphate glass exposed to about 150r. This glass meets these requirements satisfactorily except for the intensity of the fluorescent light, which in this case is equivalent to the intensity of fluorescence of a silver phosphate glass exposed to approximately 1300r. However, this factor can be overcome by masking the u.v. exciting radiation so that the intensity of fluorescence of the manganese glass will be lowered. The glass developed (melt E-9272) has the following composition:

<u>Oxide</u>	<u>Wt.%</u>
SiO <sub>2</sub>	34.08
Na <sub>2</sub> O	23.27
B <sub>2</sub> O <sub>3</sub>	33.00
MnO <sub>2</sub>	2.50
As <sub>2</sub> O <sub>3</sub>	1.50
Sb <sub>2</sub> O <sub>3</sub>	5.65

This melt was made in a 15 inch (experimental size) clay pot in a gas-fired furnace. Since this glass may be used in large quantities and the use as a standard requires it to be uniform, two additional melts have been made - Melt C-1109 (30 inch production size clay pot) and Melt C-2710 (34 inch production size clay pot). Approximately 10,000-15,000 pieces can be obtained from C-1109 and 15,000-20,000 pieces from C-2710. These melts are identical in composition to melt E-9272. The glass was developed as a Bausch and Lomb product. Melt C-2710 was made under this contract. At present, a production order is being filled to the Admiral Corporation for this glass for use in the CP-95/PD field reader. The standard glass, for standardization purposes, is referred to as : "E-9272."

1.3.3.2 Factors affecting the Fluorescent Property

Since the intensity of fluorescent light of this glass is too high to be read on the CP-95(XN-3)/PD, a shield was made to fit into one of the sample stations in the swinging sector of the sample support system. In this position, the shield was between the ultraviolet source and the sample being measured. The shield completely covered the opening in the sample station except for 9 holes (.116 inches in diameter) drilled in the shield that were centered and equally spaced in the opening. All readings listed in Appendix VI, VII, VIII, and IX on this glass were taken with this shield in place. The glass was prepared for reading in the following manner -  
Size (average) - .728" x .728" x .178"

Finish - 1 edge (designated as exit edge) - No. 320  
grit grind

2 faces and 3 edges ( 1 face designated  
as u.v. face) - No. 120 grit grind

1 face and 3 edges (other than exit edge  
and u.v. face) were painted with non-fluorescing  
black lacquer.

1.3.3.2.1 Variation Within a Melt

Twenty random samples were taken from the cast sheet of  
Melt C-1109. The readings are listed in Appendix VI.  
The average calculated intensity of fluorescence on the  
20 random samples (see column 4 of Appendix VI) is 1295  
Roentgens with an average deviation from the mean of  
1.4%. Also noteworthy is the fact that there appears  
to be no correlation between volume of glass and intens-  
ity of fluorescence as it pertains to the normal varia-  
tions in volume obtained in finishing operations.

1.3.3.2.2 Normal Variations in Manufacturing of the Finished Pieces  
From the Melt

Nineteen samples were selected from a production run  
(Admiral Order), using melt C-1109, that were the widest  
variation in color of the glass. Color is a rough indi-  
cation of the fluorescent nature of this glass. The  
normal procedure in manufacturing after the melt is cast  
is to cut the sheet into squares of a certain pre-deter-  
mined weight, press the pieces in a gas-fired pressing  
furnace into a shape that can be easily machined to fin-  
ished dimensions, and anneal in a gas-fired lehr with  
a schedule as follows: - start - 1000°F, reduce to 900°F -

1 hr., reduce to 800°F - 2 hr., reduce to 700°F - 2 hr., Total time - 11 hrs. The readings are listed in Appendix VII. The average deviation from the mean of 3.1% represents the maximum tolerance that can be expected in normal manufacturing of these pieces.

1.3.3.2.3 Extreme Variations in Manufacturing of the Finished Pieces From the Melt

For this experiment, 20 additional samples were taken from Melt C-1109. The variables that occur in manufacturing were deliberately over-emphasized, so that these factors could be fully evaluated. The samples were divided into 4 groups as follows -

Group-1 - Cut pieces from the cast sheet were annealed in a continuous gas lehr. Schedule: - start - 900°F, reduce to 800°F, 2 hrs., reduce to 700°F - 2 hrs., Total Time - 10 hrs.

Group-2 - Cut pieces from the cast sheet were annealed in a continuous gas lehr - Schedule: - start - 1000°F, reduce to 900°F - 1 hr., reduce to 800°F - 2 hr., reduce to 700°F - 2 hr., Total Time 11 hrs.

Group-3 - Cut pieces from cast sheet were annealed in a gas-fired kiln. Schedule: - start - 950°F - 12 hr., reduce 2.5°F/hr to 900°F, reduce 5.0°F/hr to 800°F, reduce 7.0°F/hr to 700°F, Total time - 48 hrs.

Group-4 - Cut pieces from cast sheet were pressed in gas-fired pressing furnace, annealed in continuous gas lehr (same schedule as Group-2), and reannealed in gas-fired kiln (same schedule as Group-3).

The readings are listed in Appendix VIII. From this table it is quite evident that the variation in intensity of fluorescence due to various heat treatments is considerable, varying approximately 25% between Group-1 and Group-4. Comparing Group 4 in Appendix VIII with Appendix VI, it is also noted that the average deviation from the mean is reduced considerably by a long heat treatment.

1.3.3.2.4 Variation Between Melts

Thirty samples each from Melts G-1109 and C-2710 were used for this evaluation and were divided into 2 groups as follows -

Group-1 - Ten samples from each melt were pressed in a gas-fired pressing furnace and annealed in an electric lehr with the following schedule: - start -950°F, reduce to 850°F - 1 hr., reduce to 750°F-2 hr., Total Time - 6 hrs.

Group-2 - Twenty samples from each melt were pressed in a gas-fired pressing furnace, annealed in an electric lehr with same schedule as Group-1 samples, and reannealed in Homo-type annealing furnace with the following schedule : hold-950°F 48 hrs., cool - 86°F/hr.

The readings are listed in Appendix IX. Group-1 consists of the direct comparison of the two melts with normal processing schedules. Group-2 consists of readings on samples where it was hoped to cancel previous thermal history and stabilize the fluorescence of the glasses. Group-1 readings indicate that Melt C-2710

has approximately 4.5% more fluorescence than Melt C-1109, and Group-2 readings indicate that Melt-C-2710 is 10.5% higher. Since Melt C-2710 is a larger melt than C-1109, some of this difference may be due to size. However since a much smaller average deviation from the mean was obtained on any one given group of samples with gas-fired kiln annealing, (see Group-4, Appendix VIII) some of the difference may be due to electric instead of gas annealing.

#### 1.3.4 Direct Reading Dosimeter Glass

By a direct reading dosimeter is meant a dosimeter that indicates through the change of visible color induced by the radiation. The radiation may introduce different colors to an initially colorless glass, or may bleach out the color originally existing. The color production is usually caused by formation of color centers in glass as discussed by Sun and Kreidl (5) and by Mayer and Gueron (6). This is a very important consideration in dosimetry. Sometimes formation of coloring ions through the oxidation or reduction effect of radiation is also responsible for the color production. For example, a colorless  $Mn^{++}$ -containing glass yields a purple color due to the formation of  $Mn^{+++}$  upon exposure to radiation. The color bleaching is carried out by the change of the oxidation-reduction state of any coloring ions or atomic groupings. One example is the blue sulfur glass suggested by Otley and Weyl et.al.(7) which is bleached by the action of radiations. The

blue color is due to some poly-atomic grouping of sulfur which is oxidized to colorless  $S^{--}$  by the radiations. According to Friedman and Glover (3), the visibility threshold for F-centers in alkali halide crystals is about  $10^{14} - 10^{15}$  F-centers per  $cm^3$ . This corresponds to 10 - 100r. If this is true also for glass, then the sensitivity for the direct colorimetric method cannot be pushed very much below 10r. The method suffers an intrinsic difficulty. The situation in the formation or destruction of colors due to oxidation or reduction of ions is not known. It is reasonable to assume that the threshold dosage for visibility would be about the same order as that for color center formation. Experimental evidences seem to indicate that this is true.

It would not be profitable to investigate a direct reading dosimeter sensitive to radiation below 10r unless a means of amplification of the radiation effect is found.

Theoretically there are at least two ways to achieve the amplification. The first is through a chain reaction. The effect of radiation is merely to initiate the chain. AgBr crystals in photography are developable after one or two atoms of Ag in the crystal are reduced. The second is through the effect of nucleation. This is the well-known phenomenon in a cloud chamber. The radiation produce charged ions which serve as the centers of nucleation for condensation of vapor. By this means a single nuclear particle is made visible. The



general idea may be carried over into glass, although the situation is somewhat different. Rindone and Weyl (8) have found that devitrification or phase separation of glass is accelerated through the presence of Pt or other atoms. It is conceivable that any atomic Ag, Au, Pt, (or other elements) reduced through the effect of radiation in a glass, may serve as the centers of nucleation. If the glass after exposure to the radiation is heated to obtain the phase separation around these nuclei, it might be possible that an amplified visible effect would result from small dosages. These amplification effects should be investigated with great vigor.

In the present investigation the study of the amplification effect is limited by time. The emphasis was on color center formation and color bleaching for direct reading. A brief survey was also made on the problem of phase separation. These studies are described as follows:

1.3.4.1 Tenebrescence Through Color Center Formation

1.3.4.1.1 Glasses of the Composition of the Radiophotoluminescent Dosimeter Glass with Small Additions:

In the early work with the radiophotoluminescent phosphate glass containing silver it was observed, especially by Schulman et.al. (2), that a yellow coloration developed under prolonged exposure to gamma rays. The present writers observed later that the addition of certain elements that enhanced radiophotoluminescence,

also appeared to increase this direct coloration. Small scale experiments indicated that 100r exposures might be visually detected through 1" thicknesses of glasses to which e.g. 0.02%Pt, 0.005%Ir, 0.005% Au, 0.5% KI, 1.0% BaF<sub>2</sub>, or 0.1% NH<sub>4</sub>SCN had been added. This indication was verified when two pounds of a glass containing:

50 parts Al (PO<sub>3</sub>)<sub>3</sub>  
25 parts Ba (PO<sub>3</sub>)<sub>2</sub>  
20 parts KPO<sub>3</sub>  
5 parts KNO<sub>3</sub>  
8 parts AgPO<sub>3</sub>  
1 part BaF<sub>2</sub>

(i.e. the radiophotoluminescent glass, with a small substitution of (NO<sub>3</sub>)<sup>-</sup> for (PO<sub>3</sub>)<sup>-</sup> and the addition of 1 part BaF<sub>2</sub>) was melted in a zircon crucible. The sample dimensions were 39 x 48.5 x 57 mm. Two 39 x 48.5 mm faces were polished, the other four sides ground to #80 grit finish and then painted with black paint. Readings were taken of the absorption bands formed in the visible spectrum after exposures of 20, 40, 80, 160, 320, 640 r on a Hardy Recording Spectrophotometer and a Hunter Color - Color-Difference Meter (10). Both instruments gave a measurable change after 20 r and a fairly linear curve of absorption resulted after subsequent exposures. The results are shown in Figures 1, 2, and 3. A visible change was detected on exposed samples at the 80 r level. All these findings are rather unique at the present stage of knowledge. A control sample was used on all readings. The color change could be enhanced by

greater thickness and by using an integrating device such as coating a long cylinder with white paint and enclosing this assembly in an opaque container so that only one surface would be exposed. This suggestion was made by Dr. J. Schulman of the Naval Research Laboratory. Undoubtedly some of the glasses also have developed u.v. absorption. If u.v. radiations are allowed to pass through the glass under study, and detected by means of an efficient green phosphor, the decrease in fluorescence may be noted for glasses that have developed absorption centers in the u.v. region. The direct coloration of some of these glasses may be useful in a direct-reading dosimeter if greater sensitivity can be obtained. However, the color change obtained on most glasses in this phase are in the most insensitive portion of the spectrum, namely a yellow coloration.

1.3.4.1.2 Other Phosphate Glasses:

Soon after the radiophotoluminescent type dosimeter was introduced, it was discovered that the K-Ba-Al phosphate base glass developed a purple color upon irradiation with gamma rays. The color was probably due to the formation of color centers. Initial results obtained during the present study also indicated that this direct coloration has been enhanced by the additions of  $As_2O_3$  - 10%, KI - 5%,  $BaF_2$  - 50%. The glass containing 5% - KI was observed to darken after 300 r exposure. The glasses containing  $As_2O_3$  and  $BaF_2$  indicated a color change after 600 r exposure.

Next, a composition variation of the K-Ba-Al phosphate glass was made. This composition was: -  $\text{KPO}_3$  50% by wt.,  $\text{Al}(\text{PO}_3)_3$  25% and  $\text{Ba}(\text{PO}_3)_2$  25%. A visual observation of this glass through a 1" thickness after 2000 r exposure indicated a darkening. Attempts were made to sensitize this reaction by treating the glass. An unexposed sample of the glass was treated with 10% HCl for 4 hrs. and then exposed. This treatment had no apparent effect on the sensitivity. A second sample of unexposed glass was heated to  $350^\circ\text{C}$ . in an  $\text{H}_2$  atmosphere. The glass darkened during this treatment; however, the sensitivity to gamma rays was not changed appreciably. Additions of equal amounts of  $\text{MnO}_2$  and  $\text{As}_2\text{O}_5$  were made in concentrations of 0.01%, 0.1%, 1%, 2%, and 4% to this revised base glass. Those with 0.01% and 0.1% both exhibited a darkening after 2000 r exposure. The glasses made with the other additions did not show a change after 2000 r exposure.

Other glasses made that are revisions to the dosimeter base glass include an addition of 0.001%  $\text{TiO}_2$  / varying amounts of  $\text{AgPO}_3$  - 2%, 4%, 12%, 16%. A color change was detected through a 1" thickness on these glasses after 600 r exposure. The glass containing 16%  $\text{AgPO}_3$  may have a yellow color apparent to the eye after 100 r exposure. All of the glasses in this series exhibited high fluorescence sensitivity. An additional series of glasses were made that contained alkali variations

(K,Na,Li) of the silver phosphate dosimeter glass with 12%  $\text{AgPO}_3$  instead of 8%. These glasses indicated a color change after 600 r exposure. Additional experiments with phosphate glasses include additions of 10%  $\text{Fe}_2\text{O}_3$ , 0.01% pt, 0.005% Au, (1%  $\text{Ag}_2\text{O}$ , -0.1% KBr, -0.1%  $(\text{NH}_4)\text{SCN}$ ), (10%  $\text{Ag}_2\text{O}$ , -1% KBr, -0.1%  $(\text{NH}_4)\text{SCN}$ ), to the K-Al-Ba-phosphate base glass. The glass to which  $\text{Fe}_2\text{O}_3$  was added did not show a change after exposure, as this large amount of  $\text{Fe}_2\text{O}_3$  caused the glass to be opaque. The glass containing additions of ( $\text{Ag}_2\text{O}$ , -KBr, -  $(\text{NH}_4)\text{SCN}$ ) showed a change after an exposure of 600 r. The glasses containing 0.01% Pt and 0.005% Au have been exposed to 300 r without an apparent color change. However, these glasses exhibit a slight orange fluorescence with u.v. excitation similar in color to an exposed silver-containing phosphate dosimeter glass indicating possibly that they may have the property of radiophotoluminescence, but at a much lower level of sensitivity. An exposure to 500 r indicates a very small, if any, change using the present reader.

#### 1.3.4.1.3 Borate Glasses:

A series of glasses was made by incorporating 0.1%  $\text{Ag}_2\text{O}$ , 0.1%  $\text{TiO}_2$  or 0.05% Pt to a base glass of the  $\text{Li}_2\text{O}$ - $\text{BeO}$ - $\text{B}_2\text{O}_3$  type. Definite color changes were noticed in the Ag and Ti containing glasses after 600 r exposure. The glass containing Pt did not show any apparent changes. For details on glasses made in the study of color center formation see Appendix X. From these experiments, it

is obvious that direct color changes can be detected with radiation dosage as low as 10 r. However, it should be noted that the color change is very slight even in a sample 1" thick. Further investigation is necessary.

1.3.4.2 Tenebrescence Through Radiation Bleaching

Otley and Weyl (7) obtained a blue glass by adding elementary sulfur to a sodium-borate batch. The blue color is ascribed to the polyatomic sulfur groups which are reduced to colorless S<sup>-</sup> ions upon irradiation with x-rays. An attempt was made to reproduce the effect by exposing such a blue glass to 2000 r of gamma radiation. No bleaching of color was observed. (This glass has an orange fluorescence when excited with u.v.) The experiment was repeated with similar results. Since the composition, container, and schedule used were very similar to those used in Otley's and Weyl's experiments, their results will most likely have to be attributed to softer radiation. Several experiments were made with sulfur-borate glasses of varying compositions. Additions of NaF, KF, LiF, and Al<sub>2</sub>O<sub>3</sub> were made in varying amounts to sulfur containing borate melts. The resultant glasses were exposed to 3000r or more without apparent bleaching. Additional experiments included additions of Na<sub>2</sub>Se, KI, and NaF to a base glass of fused borax and fused boric acid; and additions of KBr, and Cu<sub>2</sub>Br<sub>2</sub> to fused boric acid. After an exposure of 600 r, no change was observed in these glasses. An attempt was made to develop a

blue sulfur-phosphate glass similar to the blue sulfur-borate glass. Such a glass did not result from the few experiments made. The additions of sulfur to simple phosphates such as  $\text{Ba}(\text{PO}_3)_2$ ,  $\text{Ca}(\text{PO}_3)_2$  and  $\text{Al}(\text{PO}_3)_3$ -NaF,  $\text{Al}(\text{PO}_3)_3$ -KF, and to the dosimeter base glass (K-Al-Ba) - phosphate were attempted. These glasses, some of which devitrified, did not show a reaction to gamma rays after exposures of 2000 r.

Incorporation of sulfur in silicate type of glasses was not successful. For details on glasses made in the study of color bleaching see Appendix XI.

In view of these experiments, the bleaching type of glasses does not seem to be promising as a dosimeter.

#### 1.3.4.3 Miscellaneous Study:

A glass in the system  $\text{Li}_2\text{O}-\text{BeO}-\text{B}_2\text{O}_3$  was made in order to observe the effect of radiation on devitrification. A 600 r exposure to gamma rays gave no indication of any change. Perhaps the glass should be heat treated in order to promote devitrification.

#### 1.3.5. Thermoluminescent Glass

Unless the effect of amplification of radiation in the direct reading dosimeter can be realized, the chance of detecting dosages in the range  $10^{-3}$  - 10 r lies in the field of thermoluminescent glass. This point has been emphasized in the previous report by Sun and Kreidl (5). Since then, it has been known that by the thermoluminescence in crystals such as Fonda-phosphor (ZnS type) and Ag a activated NaCl, dosages in the order of  $10^{-4}$  -  $10^{-3}$

can be detected. In the glass field, its importance is only gradually realized. The thermoluminescent phenomenon takes advantage of the energy storage capacity of a crystal or a glass. When a substance is irradiated with atomic radiations, a certain amount of energy is absorbed and stored for a considerable length of time. The stored energy can be released in the form of visible or ultraviolet light by irradiation with visible or infra-red light or by heating. A disadvantage of this type of dosimeter is that once the stored energy or the dosage is measured, the record is destroyed. This is not the case for the photoluminescent or direct colorimetric dosimeters. Because of the limitation in time, the present investigation covers only a qualitative feature of the phenomenon. Further investigations are very much needed which may develop into some result of significance. The experiment to determine thermoluminescence was as follows:

The glass samples were placed in a small annealing oven that had a pyrex window (in future experiments, this should have a pure  $\text{SiO}_2$  window). The experiments were carried out in a semi-dark room. The oven was heated at a roughly uniform rate of  $6^\circ\text{C}/\text{min.}$  until a temperature of over  $300^\circ\text{C}$  was reached. The samples were observed visually while being heated. The emission of light was observed visually. It is believed that by suitable instrumentation, such as the use of a photomultiplier as the light detecting means, the sensitivity of the study can



be improved greatly.

Most of the glasses made under this contract that were different in composition have been tested in this equipment to see if they exhibited the property of thermoluminescence. One glass, melt No. 1A4055 (composition  $\text{-KPO}_3$  - 50%,  $\text{Al(PO}_3)_3$  - 25%,  $\text{Ba(PO}_3)_2$  - 25%,  $\text{MnO}_2$  - 0.1%,  $\text{As}_2\text{O}_3$  - 0.1%) did emit enough light to be seen with the eye. This glass was exposed to 2000r of gamma rays. It was observed to give off a faint near-white glow when  $200^\circ\text{C}$  was reached. The light persisted to  $300^\circ\text{C}$ ., at which point, the light completely disappeared. The same sample was again exposed, this time to 500 r, and heated again in a similar manner. The light was observed from the sample at the same temperature range but the amount was much smaller. It is likely that with better instrumentation, the limit of dosages can be pushed further down.

An attempt to produce a thermoluminescent glass reported by Nyswander and Cohn (9) was not successful. This glass was reported to exhibit this property after short exposures to daylight. The composition reported was a  $\text{ZnO-B}_2\text{O}_3$  (45.5% and 54.4% respectively) with an addition of a small amount of  $\text{ThO}_2$ . The glasses made did not appear to exhibit this property after gamma ray exposures to direct sunlight when measured in the equipment described above. No visible emission of light was observed. This may be due to the fact that our method of detection was too crude. It also indicates that the thermoluminescent glass discovered by this investiga-

tion as described may be of a more sensitive type.

Further investigations are very much needed.

#### 1.4 Conclusions

##### 1.4.1 Radiophotoluminescent Glass

The impurity level of the raw materials is the main controlling factor affecting the dosimeter properties of this glass. Other base glasses containing silver were found to have properties similar to the potassium-barium-aluminum-phosphate glass, but were no marked improvement. Several elements in near-trace concentration were found to have a sensitizing effect on this glass. The chemical reaction induced in this glass by exposure to X or gamma radiation is reversible by heating the glass at its annealing temperature.

##### 1.4.2 Manganese - Containing Standard Glass

A glass was developed to production size melting that meets the requirements of a calibration standard for the CP-95(XN-3)/PD when a shield is used in conjunction with it.

##### 1.4.3 Tenebrescent (Direct-Reading) Dosimeter Glass

Three approaches were investigated in the field of direct-reading glasses or those that undergo a visible change as a result of X or gamma radiation. These approaches were -

- 1) Color center formation
- 2) Color bleaching
- 3) Visible change as a result of devitrification

In the field of color center formation, a glass was made (containing a 1.0% addition of  $\text{BaF}_2$  to the radiophotoluminescent glass) that gave a measurable change with instruments after a 20 r exposure and a visible change (to a trained observer) after 80 r exposure through a 57 mm thickness. This type was the most sensitive direct-reading glass found. In the field of color bleaching, no glasses were found that had sensitivities in the range of personnel dosimetry (0-600 r). The hope of obtaining a glass that would show devitrification or crystal growth as a result of X or gamma radiation also was not realized.

#### 1.4.4 Thermoluminescent Glass

A phosphate glass containing small amounts of manganese and arsenic was found to exhibit this property after a 500 r exposure. The effect was observed visually in crude equipment and it is believed with instrumentation that this glass would be a sensitive detector.

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2.

PART II

RECOMMENDATIONS

- 2.1 The present investigations indicate that further work should be vigorously pursued.
- 2.1.1 In the case of radiophotoluminescent silver-containing glasses, the discovery of the effect of small amounts of "impurities" should be studied further in better controlled conditions and on more of a quantitative basis.
- 2.1.2 The search of a method to amplify the effect of radiations in the direct reading dosimetry may lead to results of basic significance.
- 2.1.3 Thermoluminescent glass should also be studied with vigor. At present, this seems to be the promising avenue in obtaining a glass sensitive to a dosage smaller than one roentgen.

# PART III

## APPENDIX I

### Various Factors Affecting the Luminescent Property of the Silver Phosphate Dosimeter Glass

Meta Phosphates of Al Ba K Ag		Variation	Readings **		Remarks
			Pre-Dose	Sensitivity	
*E A A C	1 - Melting time at 1250°C				
	10 min. 2 hrs.		Silver ppt. 62	1.19	The shorter melting time did not allow the Ag to be combined in glass
A A A A	1-1/2 hrs. 1 hr		66 20	.75 .75	The effect of a too long melting time is evident here. Apparently reduction of oxygen content of melt reduced silver out.
F C D A	2 - Melting temp. - 3 hrs. hold		65 31	.71 .80	The effect of too high a melting temp. is similar to a too long schedule.
F A D A	3 - Melting Container -1250°C 3 hrs.	Clay Pot Zircon Pot	98 127	.75 .82	Impurity contamination is believed to account for variation in properties with different melting container.
E A A A	4 - Melting Atmosphere-1200°C 1-1/2 hrs.	Electric Glo-Bar Furnace Gas Muffle Furnaced	61 Over 5000	1.17 -	A reducing atmosphere has similar effect on glass as a too low oxygen content

\* Letters designate different lots of these materials.

\*\* See paragraph 1.2.4

## APPENDIX II

### The Effect of Raw Material Variations on the Initial Fluorescence and Sensitivity of the Silver Phosphate Dosimeter Glass

Meta Phosphate of		Readings		Remarks
Al	Ba K Ag	Pre-Dose	Sensitivity	
Other				
<u>1. Aluminum Metaphosphate Variations</u>				
A A A A		66	.76	Large variation in sensitivity between lots D and E is believed to be chiefly due to iron impurity. Lot E is laboratory grade material and Lot D was old commercial grade material.
B A A A		31	.52	
C A A A		23	.43	
D A A A		12	.06	
E A A A		20	1.50	
<u>2. Potassium Metaphosphate Variations</u>				
E A B B		20	1.15	The high pre-dose obtained with lot C is believed due to a variation of the K to PO <sub>3</sub> ratio causing an oxygen deficiency.
E A C B		Over 600		
E A D B		72	1.63	
<u>3. Barium Metaphosphate Variations</u>				
F A D A		34	1.46	Lot B is believed to have slightly less iron contamination.
F B D A		32	1.62	
<u>4. Silver Metaphosphate Variations</u>				
E A A B		200	1.30	
E A A A		20	1.50	
<u>5. Improvement by Silver Nitrate</u>				
E A E B		Ag ppt.		Lot E KPO <sub>3</sub> is a hydrated phosphate. Silver added as silver nitrate in 2nd melt showing effect of oxygen content on pre-dose.
E A E -	AgNO <sub>3</sub>	22	1.54	

# APPENDIX II

(Continued)  
Page 2

Meta Phosphate of Al Ba K Ag	Other	Readings		Remarks
		Pre-Dose	Sensitivity	
E A A A E A A A	✓.02% Fe <sub>2</sub> O <sub>3</sub>	20	1.50	6. <u>Impurities Added</u> a) Iron addition shows effect on sensitivity
		28	.54	
E A B A E A B A	✓.01% Mn <sub>2</sub> O <sub>3</sub>	20	1.52	b) Manganese addition shows effect on pre-dose
		200	1.50	



APPENDIX III

Readings on Some Silver Phosphate Glasses that  
Contain Sensitizing Elements

<u>Melt Number</u>	<u>Additions</u>		<u>Readings</u>		<u>Increase in Sens.</u>
	<u>Oxide</u>	<u>Wt. %</u>	<u>Pre-Dose</u>	<u>Sens.</u>	
Frit from 1A3808	-	-	20	1.45	-
1A3987	TiO <sub>2</sub>	.001%	25	2.00	40%
1A4098	Sb <sub>2</sub> O <sub>3</sub>	.01%	23	1.77	22%
1A4101	As <sub>2</sub> O <sub>3</sub>	.01%	27	1.78	22%
1A4116	TiO <sub>2</sub>	.001%	46	1.84	28%
	ZrO(PO <sub>3</sub> ) <sub>2</sub>	.1 %			
1A4143	BaF <sub>2</sub>	.01 %	40	1.75	20%
1A4235	CeO <sub>2</sub>	.01 %	80	1.90	22%

NOTE: The base glass consists of frit from melt 1A3808 (4" zircon melt) or equiv., of which the properties had been measured. This base glass consists of:

Al(PO <sub>3</sub> ) <sub>3</sub>	- 50 parts
Ba(PO <sub>3</sub> ) <sub>2</sub>	- 25 parts
KPO <sub>3</sub>	- 25 parts
AgPO <sub>3</sub>	- 8 parts

The additions were made to this frit, which in most cases necessitated pre-mixing because of amount added, and the resulting mixture was melted at 1100°C. for 2 hours in a 2" zircon crucible. Control melts of the frit were made to gather data on the change in the initial fluorescence and the sensitivity due to the small additions.

#### APPENDIX IV

### Summary of Work on Spectrographic Analysis of Silver-Phosphate Glass and Raw Materials

#### Abstract

A method was found to quantitatively determine impurity levels in the silver phosphate glass and raw materials. The iron content in a target glass is determined as 0.005%.

#### Spectrographic Work

Object: To quantitatively determine the iron content in silver-phosphate glass and to provide a preliminary method for further work on the analysis of trace elements in raw materials and in glass.

Equipment:

1. Spectrograph
2. Excitation Source (220 V D.C.)
3. Water cooled Electrode Holder
4. Densitometer and other Accessory Items.

Standards: None commercially available. For preliminary work, a glass (melt No. 1A4105) showing target performance, was selected and various concentrations of iron were added in solution form to this glass in powder form (pass 100 mesh).

Procedure: In accordance with standard procedures for the analysis of powdered materials, the powdered glass was mixed with powdered graphite and a buffer material (CuO). The mixture was added to graphite electrodes and was excited to obtain a spectrum.

Experimental Work: From preliminary results, it was found that the buffer material contained more iron than the glass. To overcome this, several experiments with wet method chemistry were made to purify the CuO. (Purified CuO in powder form is not available commercially). The experiments may be summarized as follows:

- a) Oxalic acid was added to a solution of copper ammonium chloride to ppt. copper oxalate. The ppt. was converted to CuO by heating. A spectrogram of this material still showed iron.
- b) A ppt. of  $\text{Fe}(\text{OH})_3$  was filtered off from a solution of copper ammonium chloride in alkaline medium. The pH was lowered and copper oxalate ppt'd. The copper oxalate was then converted to CuO by heating. A spectrogram taken of this material showed a considerable removal of iron, but content still too high (approx. 0.01%).

APPENDIX IV  
(Continued)  
Page 2

To avoid purification problems, a spectrogram was taken of other available buffer materials:

- a) ZnO
- b) PbO
- c) Zn Powder
- d)  $\text{Sb}_2\text{O}_3$

The results indicated that the PbO and  $\text{Sb}_2\text{O}_3$  contained considerable iron. The ZnO and Zn powder showed a very small trace of iron (less than 0.001%). Therefore, these materials were tried as a buffer material. The ZnO did not prove to be satisfactory since its hygroscopic tendency made it difficult to use. However, the Zn metal powder worked.

Results: Using this material as a buffer in conjunction with water-cooled electrodes, a working curve was obtained with the target glass and iron additions to this, as described under standards. By extrapolation from this curve, the level of iron impurity in this "target" glass is 0.005%.

Conclusions: From this ground work, it is believed that the procedure will be applicable to other components in the glass and raw materials.

APPENDIX V

Testing of Radiophotoluminescent Glass Under Specification MIL-D-16153C (Ships)

Storage Par. 3.6.1

Test Conditions	Experimental Data					Comments
	<u>Predose</u>					
	<u>*Sample</u>	<u>Initial</u>	<u>After Storage</u>	<u>**Exposure(r)</u>	<u>Sensitivity</u>	
1. Read predose	T-41	43	58	525	.94	The glass elements were stored outside of the DT-60()/PD Cases, since there were no cases available at the time of testing. This is believed to be the cause of increase in predose readings after storage. The sensitivity was not affected by this storage.
2. Hold at -55°C-24 hrs.	T-42	36	49	525	.92	
3. Hold at +85°C-24 hrs.	T-43	40	58	20	.85	
4. Read predose	T-44	38	52	20	.90	
5. Expose 2 samples to 525r	T-45	35	48	20	.95	
6. Expose 3 samples to 20r						
7. Read postdose						

## APPENDIX V

Testing of Radiophotoluminescent Glass Under Specification MIL-D-16153C (Ships)Exposure Temp. - Par. 3.6.2

Test Conditions	Experimental Data					Comments
	Sample	Predose	Dose (r)	Exposure Temp (°F)	Sensitivity	
1. Read Predose  2. Expose 5 samples each at 55°, 60°, 80°F  3. Read Postdose	T-1	31	20	80	1.00	In this small temperature difference there is barely a detectable change in response of the glass, since the variation between samples absorbs most of the differential. However, there is an indication that samples exposed at 55°F have a lower response than those exposed at 80°F. See Fig. 4.
	T-2	31	75	80	.95	
	T-3	33	150	80	.99	
	T-4	34	150	80	.97	
	T-5	30	500	80	.90	
	T-6	30	500	60	.93	
	T-7	30	500	60	.92	
	T-8	31	500	60	.92	
	T-9	38	500	60	.91	
	T-10	32	500	60	.90	
	T-11	37	20	55	1.05	
	T-12	37	75	55	.89	
	T-13	32	150	55	.87	
	T-14	32	200	55	.85	
	T-15	33	500	55	.85	

## APPENDIX V

Testing of Radiophotoluminescent Glass Under Specification MIL-D-16153C (Ships)Reading Temp. - Par 3.6.3

Test Conditions	Experimental Data						Comments
	Sample	Pre-Dose	(r) Exposure	Read at 70°F	Sensitivity Change Temp. to (°F)	Read at New Temp.	
1. Read predose	T-46	37	500	.96	75	.96	The samples were exposed to the various levels as indicated and then read under normal conditions
2. Expose to various levels	T-47	37	20	.85	75	.85	
	T-48	38	50	.96	75	.96	
	T-49	37	100	.93	75	.97	
	T-50	38	200	.93	75	.90	
3. Read postdose							The sample temperature was changed and reading taken as soon as possible after removing from icebox or oven
4. Change temperature of samples and reread	T-51	40	500	.97	65	.98	
	T-52	38	20	.95	65	1.00	
	T-53	41	50	1.00	65	.98	
	T-54	40	100	.91	65	.97	
	T-55	40	200	.92	65	.94	
	T-56	42	500	.96	20	1.16	The readings show a fairly linear response as can be seen from Fig. 5.
	T-57	40	20	.95	20	1.60	
	T-58	40	50	.96	20	1.44	
	T-59	39	100	.91	20	1.29	
	T-60	40	200	.92	20	1.22	
	T-61	41	500	.94	140	.70	
	T-62	41	20	1.00	140	.35	
	T-63	30	50	.98	140	.60	
	T-64	35	100	.94	140	.63	
	T-65	31	200	.92	140	.60	

APPENDIX V

Testing of Radiophotoluminescent Glass Under Specification MIL-D-16153C (Ships)

Minimum Dose - Par. 3.8.2-

Test Conditions	Experimental Data				Comments
	<u>Sample</u>	<u>Predose</u>	<u>Exposure(r)</u>	<u>Sensitivity</u>	
1. Read predose	TT-41	32	10	.90	
2. Expose to 10r	TT-42	39	10	1.00	
3. Read postdose	TT-43	35	10	.80	
	TT-44	31	10	.90	
	TT-45	37	10	1.10	

APPENDIX V

Testing of Radiophotoluminescent Glass Under Specification MIL-D-16153C (Ships)

Accuracy - Par. 3.8.3.1

Test Conditions	Experimental Data				Comments
	<u>Sample</u>	<u>Predose</u>	<u>Exposure(r)</u>	<u>Sensitivity</u>	
1. Read predose	T-21	41	10	1.10	
	T-22	32	10	1.10	
	T-23	32	10	1.10	
	T-24	33	10	1.10	
2. Expose to various levels	T-25	43	50	.96	
	T-26	38	50	.95	
	T-27	33	50	.94	
	T-28	36	50	.92	
3. Read postdose	T-29	33	115	.91	
	T-30	34	115	.91	
	T-31	37	115	.84	
	T-32	32	115	.91	
	T-33	38	200	.91	
	T-34	35	200	.90	
	T-35	37	200	.86	
	T-36	40	200	.90	
	T-37	38	500	.92	
	T-38	33	500	.91	
	T-39	43	500	.92	
	T-40	31	500	.92	



# APPENDIX V

Sheet (6) of 10

## Testing of Radiophotoluminescent Glass Under Specification MIL-D-16153C (Ships)

Persistence - 3.8.3.2

Test Conditions	Experimental Data				Comments
1. Read predose	Sample	Predose	Exposure(r)		The samples were stored in Humidity Chamber, Ice-box & oven without being sealed into case. This is believed to be the cause of the increase in readings when the samples were stored at high temperature & high humidity. There was a weathering film evident on the polished surfaces of the glass after Humidity storage. The tests will be repeated with the glass sealed in the DT-60()/PD cases.
2. Expose to various levels	TT-1	31	500		
3. Read postdose	TT-2	31	500		
4. Store at +140°F & 35% R.H. (Relative Humidity) - 7 days	TT-3	35	260		
5. Read	TT-4	30	260		
6. Store at -67°F 1 day	TT-5	30	105		
7. Read	TT-6	31	105		
8. Store at +140°F 1 day	TT-7	33	55		
9. Read	TT-8	30	55		
10. Store at -67°F 1 day	TT-9	34	0		
11. Read	TT-10	31	0		
12. Store at +140°F 1 day	Sensitivity				Note: Samples TT-9 and TT-10 were not exposed so, therefore have no real sensitivity. However, the nominal value of 1.0 for sensitivity was assigned to these samples for an easy comparison to the exposed samples. The samples were used as controls to show how the temperature and humidity conditions alter the surfaces of the glass but do not alter the chemical change caused by high energy irradiation.
13. Read	Sample	After 7 days	After 1 day	After 1 day	
14. Store +140°F & 50% R.H. - 1 day	TT-1	After Exposure	After 7 days	After 1 day	
15. Read	TT-2	After Exposure	After 7 days	After 1 day	
16. Store at +140°F & 95% R.H. - 1 day	TT-3	After Exposure	After 7 days	After 1 day	
17. Read	TT-4	After Exposure	After 7 days	After 1 day	
	TT-5	After Exposure	After 7 days	After 1 day	
	TT-6	After Exposure	After 7 days	After 1 day	
	TT-7	After Exposure	After 7 days	After 1 day	
	TT-8	After Exposure	After 7 days	After 1 day	
	TT-9	After Exposure	After 7 days	After 1 day	
	TT-10	After Exposure	After 7 days	After 1 day	
	Sample	After Exposure	After 7 days	After 1 day	
	TT-1	After Exposure	After 7 days	After 1 day	
	TT-2	After Exposure	After 7 days	After 1 day	
	TT-3	After Exposure	After 7 days	After 1 day	
	TT-4	After Exposure	After 7 days	After 1 day	
	TT-5	After Exposure	After 7 days	After 1 day	
	TT-6	After Exposure	After 7 days	After 1 day	
	TT-7	After Exposure	After 7 days	After 1 day	
	TT-8	After Exposure	After 7 days	After 1 day	
	TT-9	After Exposure	After 7 days	After 1 day	
	TT-10	After Exposure	After 7 days	After 1 day	
	Sample	After Exposure	After 7 days	After 1 day	
	TT-1	After Exposure	After 7 days	After 1 day	
	TT-2	After Exposure	After 7 days	After 1 day	
	TT-3	After Exposure	After 7 days	After 1 day	
	TT-4	After Exposure	After 7 days	After 1 day	
	TT-5	After Exposure	After 7 days	After 1 day	
	TT-6	After Exposure	After 7 days	After 1 day	
	TT-7	After Exposure	After 7 days	After 1 day	
	TT-8	After Exposure	After 7 days	After 1 day	
	TT-9	After Exposure	After 7 days	After 1 day	
	TT-10	After Exposure	After 7 days	After 1 day	

APPENDIX V

Testing of Radiophotoluminescent Glass Under Specification MIL-D-16153C (Ships)  
Repeat of Persistence-3.8.3.2

Test Conditions	Experimental Data				Comments
	Sample	Exposure(r)	Pre-Dose	Sensitivity Before Storage After Storage	
1. Read	T-21	10	41	1.10	Samples were taken from those used for Accuracy Test and were sealed in DT-60/PD cases
2. Samples placed in DT-60/PD cases	T-25	50	43	.96	
3. Store at 140°F & 95% R.H. - 18 hrs.	T-29	115	33	.91	
4. Drop to 80°F & bring up to 149°F & 95% R.H. in 1 hr.	T-33	200	38	.91	
5. Hold at 149°F & 95% R.H. for 5 hrs.	T-37	500	38	.92	

6. Cool to 86°F & 95% R.H. in 4 hrs.
7. Hold at 86°F & 95% R.H. for 11 hrs.
8. Cool to 68°F & 95% R.H. in 2 hrs.
9. Hold at 68°F & 95% R.H. for 4 hrs.
10. Bring to 86°F & 95% R.H. in 2 hrs.
11. Hold at 86°F & 95% R. H. for 15 hrs.

12. Repeat steps 4 through 11.  
Total Time - 112.5 hrs.

NOTE: This is cycling schedule as specified in MIL Std-150 (high temperature portion.)

# APPENDIX V

Sheet (8) of 10

## Testing of Radiophotoluminescent Glass Under Specification MIL-D-16153C (Ships)

### Additivity - Par. 3.8.3.3

Test Conditions	Experimental Data				Comments
Sample	Predose	Exposure (r)	Total	Sensitivity	
TT-11	30	150		.87	
TT-12	34	150		.89	
TT-13	32	150		.89	
TT-14	30	150		.87	
TT-15	33	150		.87	
TT-16	31	150		.87	
TT-17	32	150		.86	
TT-18	32	150		.86	
TT-19	36	150		.88	
TT-20	33	150		.88	
TT-21	38	150		.82	
TT-22	33	150		.86	
TT-23	34	150		.81	
TT-24	34	150		.83	
TT-25	32	150		.84	
3. Read postdose					

1. Read predose

2. Expose samples to 150r with various schedules -

a) Five samples(TT-11 through TT-15)exposed to a continuous dose of 150r.

b) Five samples(TT-16 through TT-20)exposed to 150r by exposing in 30r steps with 5 min delays between exposures.

c) Five samples(TT-21 through TT-25)exposed to 150r with the following schedule -

30r-hold 7 days  
30r-hold 3 days  
30r-hold 6 days  
30r-hold 4 days  
30r

3. Read postdose

APPENDIX V

Testing of Radiophotoluminescent Glass Under Specification MIL-D-16153C (Ships)

Integration Rate - Par. 3.8.3.4

Test Conditions	Experimental Data					Sensitivity		Comments
	Sample	Predose	Dose	Exposure Rate (r/hr)	Total	10 min.	4 hrs.	
1. Read predose	TT-26	34	50	25.00	150	.76	.88	
			50	6.20		-	.87	
			50	1.55		.87	.91	
2. Expose samples at various rates	TT-27	30	50	25.00	150	.78	.90	
			50	6.20		-	.88	
			50	1.55		.89	.93	
3. Read postdose	TT-28	37	50	25.00	150	.82	.88	
			50	6.20		-	.87	
			50	1.55		.89	.89	
a) 10 min. after exposure	TT-29	36	50	25.00	150	.84	.96	
			50	6.20		-	.84	
			50	1.55		.95	.97	
b) A minimum of 4 hrs. after exposure	TT-30	31	50	25.00	150	.80	.88	
			50	6.20		-	.89	
			50	1.55		.89	.91	
	TT-31	32	50	1.55	100	.94	.96	
			50	6.20		.87	.93	
			50	1.55		.88	.94	
	TT-32	38	50	1.55	100	.88	.94	
			50	6.20		.88	.94	
			50	1.55		.91	.92	
	TT-33	32	50	1.55	100	.88	.94	
			50	6.20		.91	.94	
			50	1.55		.91	.92	
	TT-34	34	50	1.55	100	.88	.96	
			50	6.20		.91	.96	
			50	1.55		.91	.91	
	TT-35	32	50	1.55	100	.90	.96	
			50	6.20		.86	.87	
			50	1.55		.86	.89	
	TT-36	39	150	6.20	150	.86	.87	
	TT-37	41	150	6.20		.87	.88	
	TT-38	39	150	6.20		.87	.89	
	TT-39	33	150	6.20	150	.87	.88	
	TT-40	33	150	6.20		.88	.89	

APPENDIX V

Testing of Radiophotoluminescent Glass Under Specification MIL-D-16153C (Ships)

NOTES:

\* The samples prefixed by the letter "T" were prepared as follows:

Size: .750" x .750" x .185"

Finish: 1 face (U.V. entrance Face) - #1200 grit grind  
1 edge (exit edge) - polish  
1 face and 3 edges - #120 grit grind

The 1 face and 3 edges having the #120 grit surface were painted with non-fluorescing black lacquer.

The samples prefixed by the letters "TT" are the same as the above samples except they were .175" thick instead of .185".

\*\* All the exposures were Co<sup>60</sup> gamma radiation.

APPENDIX VI

Variation in Intensity of Fluorescence Within a Melt

<u>Sample No.</u>	<u>Vol. of Glass(in )</u>	<u>*Reading Using Shield</u>	<u>**Calculated intensity of Fluorescence(Roentgens)</u>
1	.0955	285	1275
2	.0963	285	1275
3	.0966	285	1275
4	.0941	290	1295
5	.0950	295	1320
6	.0958	290	1295
7	.0938	295	1320
8	.0941	290	1295
9	.0949	280	1250
10	.0960	285	1275
11	.0943	295	1320
12	.0944	285	1275
13	.0941	280	1250
14	.0962	295	1320
15	.0958	290	1295
16	.0956	290	1295
17	.0956	295	1320
18	.0955	290	1295
19	.0946	295	1320
20	.0952	295	1320
M-432 (Instrument Standard)		31	138 (Reading without shield)

1295 ave.

1.4% ave.  
deviation from  
the mean

NOTES:

\* The readings were taken on CP-95(XN-3)/PD, Serial No. 19.

\*\* The calculated intensity was obtained by using as a multiplication factor, the ratio of the reading of the instrument standard-M-432 with and without the shield.

APPENDIX VII

Manganese Standard Glass

Normal Variation in Manufacturing as it effects intensity of Fluorescence

<u>Sample No.</u>	<u>Treatment</u>	<u>Reading Using shield</u>	<u>Calculated intensity of Fluorescence(Roentgens)</u>
1	(1) Pressings made	265	1180
2	in Gas-Fired		
	Pressing Furnace	300	1340
3	(2) Gas lehr annealed	290	1295
4	<u>Sched.</u> -start-1000°F		
	Reduce to	300	1340
5	900°F-1hr.		
	Reduce to	290	1295
6	800°F-2 hr.		
	Reduce to	295	1320
7	700°F-2 hr.		
	Total Time - 11 hrs.	310	1385
8		310	1385
9		300	1340
10		310	1385
11		305	1365
12		390	1295
13		320	1420
14		295	1320
15		315	1405
16		300	1340
17		280	1250
18		310	1385
19		300	1340

1335 ave.

3.1% ave.  
deviation from  
the mean

APPENDIX VIII

Manganese Standard Glass

Extreme Variation in Manufacturing as it effects Intensity of Fluorescence

<u>Sample No.</u>	<u>Treatment</u>	<u>Reading Using Shield</u>	<u>Calculated intensity of Fluorescence(Roentgens)</u>
<u>Group 1</u>	1 Gas lehr annealed	300	1340
	2 <u>Sched.</u> -start 900°F	300	1340
	3 Reduce to	300	1340 1330 ave.
	4 800°F-2hr.	300	1340 1.1% - ave.
	5 Reduce to	290	1300 deviation from the mean
	700°F-2 hr.		
	Total Time - 10 hrs.		
<u>Group 2</u>	1 Gas lehr annealed	300	1340
	2 <u>Sched.</u> -start 1000°F	305	1365
	3 Reduce to	300	1340 1360 ave.
	4 900°F - 1 hr.	305	1365 1.1% ave.
	5 Reduce to	310	1385 deviation from the mean
	800°F - 2 hr.		
	Reduce to		
	700°F - 2 hr.		
	Total Time - 11 hrs.		
<u>Group 3</u>	1 Gas-Fired Kiln annealed	355	1585
	2 <u>Sched.</u> -start 950°F-12 hr	360	1610
	3 Reduce 2.5°F/hr.	360	1610 1605 ave.
	4 to 900°F, Reduce	360	1610 0.5% ave.
	5 5.0°F/hr, to 800°F	360	1610 deviation from the mean
	F, Reduce 7.0 F/hr.		
	to 700°F		
	Total Time - 48 hrs.		
<u>Group 4</u>	1 Pressings made in Gas-	370	1655
	2 Fired Pressing Furnace	370	1655
	3 Annealed in Gas Lehr	375	1675 1660 ave.
	4 (same sched. as on Group	370	1655 0.4% ave.
	2)Reannealed in Gas-Fired	370	1655 deviation from the mean
	Kiln (same sched. as on		
	Group 3)		



Manganese Standard Glass

Variation in Intensity of Fluorescence Between  
Two Production Size Melts

Sample No.	Treatment	Reading Using Shield		Calculated Intensity of Fluorescence (Roentgens)	
		C-1109	C-2710	C-1109	C-2710
<u>Group 1</u>	(1) Pressings made	265	270	1180	1205
	in Gas-Fired	260	255	1160	1135
	Pressing Furnace	265	275	1180	1225
		270	270	1205	1205
	(2) Electric Lehr	270	290	1205	1295
	annealed.	260	260	1160	1160
	Sched. - start	260	270	1160	1205
	950°F, Reduce to	240	280	1070	1250
	850°F - 1 hr.	250	270	1115	1205
	Reduce to	250	270	1115	1205
	750°F - 2 hr.			1155ave.	1210 ave.
	Total Time - 6 hrs.			2.9%ave.	2.4% ave.
				deviation	deviation
				from the	from the
				mean	mean
<u>Group 2</u>	1 Same as Group 1	300	340	1340	1515
	2	295	335	1320	1495
	3 Homo-annealed	295	350	1320	1560
	4 For 48 hrs. -	300	340	1340	1515
	5 950°F	305	350	1365	1560
	6 Cool - 86°F/hr	300	350	1340	1560
	7	295	355	1320	1585
	8	300	340	1340	1515
	9	300	350	1340	1560
	10	305	355	1365	1585
	11	305	335	1365	1495
	12	300	335	1340	1495
	13	300	335	1340	1495
	14	300	335	1340	1495
	15	290	355	1295	1585
	16	300	350	1340	1560
	17	305	350	1365	1560
	18	300	340	1340	1515
	19	305	340	1365	1515
	20	305	350	1365	1560
				1340ave.	1535 ave.
				0.95%	2.1% ave.
				ave.	deviation
				deviation	from the
				from the	mean
				mean	

APPENDIX X

## Glasses Made in the Field of Color Center Formation (Direct Reading)

1. Additions to the Silver Phosphate Dosimeter Glass

The silver phosphate base glass was the same as described in the note of Appendix III.

<u>Additions - %</u>		<u>Exposure(r)</u>	<u>Visual Evaluation Through 1" Thickness</u>
			Key: 0 - No Change / - Slight Color // - Noticeable Color /(100) - Color Noticed at 100r
TiO <sub>2</sub>	- 0.001, 0.01, 1.0	500	0
CeO <sub>2</sub>	- 0.01, 0.1, 1.0	500	0
GeO <sub>2</sub>	- 0.001, 0.01, 0.1, 1.0 2.0, 4.0, 8.0	500 2100	0 //
SnO <sub>2</sub>	- 0.01, 0.1, 1.0	500	0
HfO <sub>2</sub>	- 0.01, 0.1, 1.0	500	0
ThO <sub>2</sub>	- 0.01, 0.1, 1.0	500	0
MnO <sub>2</sub>	- 0.01 0.1 1.0 1.5 2.0 2.5	500 1000 2000 3000 3000 5000	0 / 0 0 0 0
V <sub>2</sub> O <sub>5</sub>	- 0.01, 0.1, 1.0	500	0
Cr <sub>2</sub> O <sub>3</sub>	- 0.01, 0.1, 1.0	500	0
Co <sub>3</sub> O <sub>4</sub>	- 0.01, 0.1, 1.0	2000	0
Nd <sub>2</sub> O <sub>3</sub>	- 0.01, 0.1, 1.0	2500	//
Sb <sub>2</sub> O <sub>3</sub>	- 0.01, 0.1, 1.0	2100	//
As <sub>2</sub> O <sub>3</sub>	- 0.01, 0.1, 1.0	2100	//
PbO	- 0.01, 0.1, 1.0	500	0
NiO	- 0.01, 0.1, 1.0	2000	0
CdO	- 0.01, 0.1, 1.0	600	0

APPENDIX X  
(Continued)

<u>Additions - %</u>		<u>Exposure(r)</u>	<u>Visual Evaluation Through 1" Thickness</u>
Cs <sub>2</sub> O	0.01, 0.1, 1.0	500	0
	2.0, 4.0, 8.0	2100	✓✓
Rb <sub>2</sub> O	0.01, 0.1, 1.0	500	0
Cu <sub>2</sub> O	0.01, 0.1, 1.0	200	0
H <sub>2</sub> O	5.0, 10.0	300	✓
Se	0.01, 0.1	2500	✓✓
	1.0	2500	0
Te	0.5	200	0
Pt	0.005, 0.02	200	✓
Ir	0.005	100	✓ (100)
Ru	0.05	100	0
Pd	0.05	100	0
Rh	0.05	100	0
Au	0.005	100	✓ (100)
BaF <sub>2</sub>	0.01, 0.1	600	✓✓
	1.0, 2.0, 4.0, 10.0, 50.0	100	✓ (100)
KHF <sub>2</sub>	25.0	300	✓✓
CuBr	0.5	200	0
KBr	1.0	100	0
KI	0.5	100	✓ (100)
(NH <sub>4</sub> )SCN	0.5, 1.0	300	0
	0.1	100	✓ (100)
(TiO <sub>2</sub> )	0.001 of each	500	✓
(Rb <sub>2</sub> O)	0.01 of each		
(TiO <sub>2</sub> )	0.001 of each	500	✓
(Cs <sub>2</sub> O)	0.01 of each		
(TiO <sub>2</sub> )	0.001 of each	500	✓
(V <sub>2</sub> O <sub>5</sub> )	0.01 of each		
(TiO <sub>2</sub> )	0.001 of TiO <sub>2</sub> with	600	✓
(ZrO)	varying amounts of ZrO (0.01, 0.1, 1.0)		

APPENDIX X  
(Continued)

Additions - %	Exposure (r)	Visual Evaluation Through 1" Thickness
(TiO <sub>2</sub> ) (CeO <sub>2</sub> ) (As <sub>2</sub> O <sub>5</sub> ) - 0.01 of each	100	0
(MnO <sub>2</sub> ) (Cs <sub>2</sub> O) - 0.01 of Cs <sub>2</sub> O with varying amounts of MnO <sub>2</sub> (1.0, 2.0, 3.0)	3000	0

2. Phosphate Glasses Other than the Silver-Phosphate Dosimeter

A. Phosphates Not Containing Silver

Composition -Wt. %	Exposure (r)	Visual Evaluation Through 1" Thickness
KPO <sub>3</sub> - 50) Al(PO <sub>3</sub> ) <sub>3</sub> - 25) Ba(PO <sub>3</sub> ) <sub>2</sub> - 25) <u>Base 1.</u>	2000	//
Base 1. <i>plus sign</i> MnO <sub>2</sub> - 0.01 As <sub>2</sub> O <sub>5</sub> - 0.01	2000	//
Base 1. <i>plus sign</i> MnO <sub>2</sub> - 0.1 As <sub>2</sub> O <sub>5</sub> - 0.1	2000	//
Base 1. <i>plus sign</i> MnO <sub>2</sub> - 1.0, 2.0, 4.0 As <sub>2</sub> O <sub>5</sub> - 1.0, 2.0, 4.0	2000	0
Al(PO <sub>3</sub> ) <sub>3</sub> - 50) Ba(PO <sub>3</sub> ) <sub>2</sub> - 25) KPO <sub>3</sub> - 25) <u>Base 2</u>		
<i>plus sign</i> As <sub>2</sub> O <sub>3</sub> - 10	500	/
Base 2 <i>plus sign</i> Fe <sub>2</sub> O <sub>3</sub> - 10	200	0
Base 2 <i>plus sign</i> KI - 5	300	/
Base 2 <i>plus sign</i> Pt - 0.01	300	0

APPENDIX X  
(Continued)

Composition - Wt.%	Exposure (r)	Visual Evaluation Through 1" Thickness
Base 2 ✓ Au - 0.005	300	0
Base 2 ✓ BaF <sub>2</sub> - 50.0	600	✓

B. Phosphates Containing Silver

Composition - Wt.%	Exposure	Visual Evaluation Through 1" Thickness
Base 2 ✓ Ag <sub>2</sub> O - 1.0 KBr - 0.1 (NH <sub>4</sub> )SCN - 0.1	600	✓✓
Base 2 ✓ Ag <sub>2</sub> O - 10.0 KBr - 1.0 (NH <sub>4</sub> )SCN - 0.1	600	✓✓
Base 2 ✓ AgPO <sub>3</sub> - 2.0 TiO <sub>2</sub> - 0.001	600	✓
Base 2 ✓ AgPO <sub>3</sub> - 4.0 TiO <sub>2</sub> - 0.001	600	✓
Base 2 ✓ AgPO <sub>3</sub> - 12.0 TiO <sub>2</sub> - 0.001	200	0
Base 2 ✓ AgPO <sub>3</sub> - 16.0 TiO <sub>2</sub> - 0.001	100	✓ (100)
Base 2 ✓ AgPO <sub>3</sub> - 13.0 CeO <sub>2</sub> - 0.1	100	✓ (100)
Al(PO <sub>3</sub> ) <sub>3</sub> - 50.0 Ba(PO <sub>3</sub> ) <sub>2</sub> - 25.0 AgPO <sub>3</sub> - 8.0	Base 3	
✓		
Rb <sub>2</sub> O - 25.0	600	✓✓
Base 3 ✓ LiPO <sub>3</sub> - 25.0	600	✓✓

APPENDIX X  
(Continued)

Composition -Wt %	Exposure (r)	Visual Evaluation Through 1" Thickness
Base 3 ✓ NaPO <sub>3</sub> - 25.0	600	✓✓
Al(PO <sub>3</sub> ) <sub>3</sub> -50.0 Ba(PO <sub>3</sub> ) <sub>2</sub> -25.0 AgPO <sub>3</sub> -12.0	Base 4	
✓		
NaPO <sub>3</sub> -25.0	200	✓
Base 4 ✓ NaPO <sub>3</sub> -25.0 TiO <sub>2</sub> -0.001	200	✓
Base 4 ✓ LiPO <sub>3</sub> -25.0	200	✓

3. Borate Glasses

Composition -Wt %	Exposure (r)	Visual Evaluation Through 1" Thickness
Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> - 70 B <sub>2</sub> O <sub>3</sub> - 15 Na Se - 15	600	0
Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> - 70 B <sub>2</sub> O <sub>3</sub> - 15 KI - 15	600	0
Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> - 70 B <sub>2</sub> O <sub>3</sub> - 15 NaF - 15	600	0
B <sub>2</sub> O <sub>3</sub> - 75) BeO - 10) Li <sub>2</sub> O - 15	Base 5 600	0
Base 5 ✓ Ag <sub>2</sub> O -0.1	600	✓✓
Base 5 ✓ TiO <sub>2</sub> -0.1	600	✓✓
Base 5 ✓ Pt -.05	600	0

APPENDIX XI

Direct Reading Glasses Made in the Field of Color Bleaching

<u>Composition - Wt %</u>		<u>Exposure (r)</u>	<u>Visual Evaluation Through 1" Thickness</u>
Key: 0 - No Change / - Slight Color // - Noticeable Color / (100) - Color Noticed at 100r			
Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	- 70		
B <sub>2</sub> O <sub>3</sub>	- 20	2000	0
S	- 10		
Ba <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	- 63		
B <sub>2</sub> O <sub>3</sub>	- 32	2000	0
S	- 5		
Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	- 70		
NaF	- 20	500	0
S	- 10		
B <sub>2</sub> O <sub>3</sub>	- 40		
KF	- 50	2500	0
S	- 10		
B <sub>2</sub> O <sub>3</sub>	- 40		
LiF	- 50	500	0
S	- 10		
B <sub>2</sub> O <sub>3</sub>	- 88	2500	0
Al <sub>2</sub> O <sub>3</sub>	- 2.0		
S	- 10		
B <sub>2</sub> O <sub>3</sub>	- 54.4		
ZnO	- 45.5	500	0
ThO <sub>2</sub>	- 0.1		
SiO <sub>2</sub>	- 66.6		
B <sub>2</sub> O <sub>3</sub>	- 11.2	2500	0
Na <sub>2</sub> O	- 22.2		
S	- 4.0		
SiO <sub>2</sub>	- 28.6		
B <sub>2</sub> O <sub>3</sub>	- 42.9		
Na <sub>2</sub> O	- 28.5	2500	0
S	- 4.0		

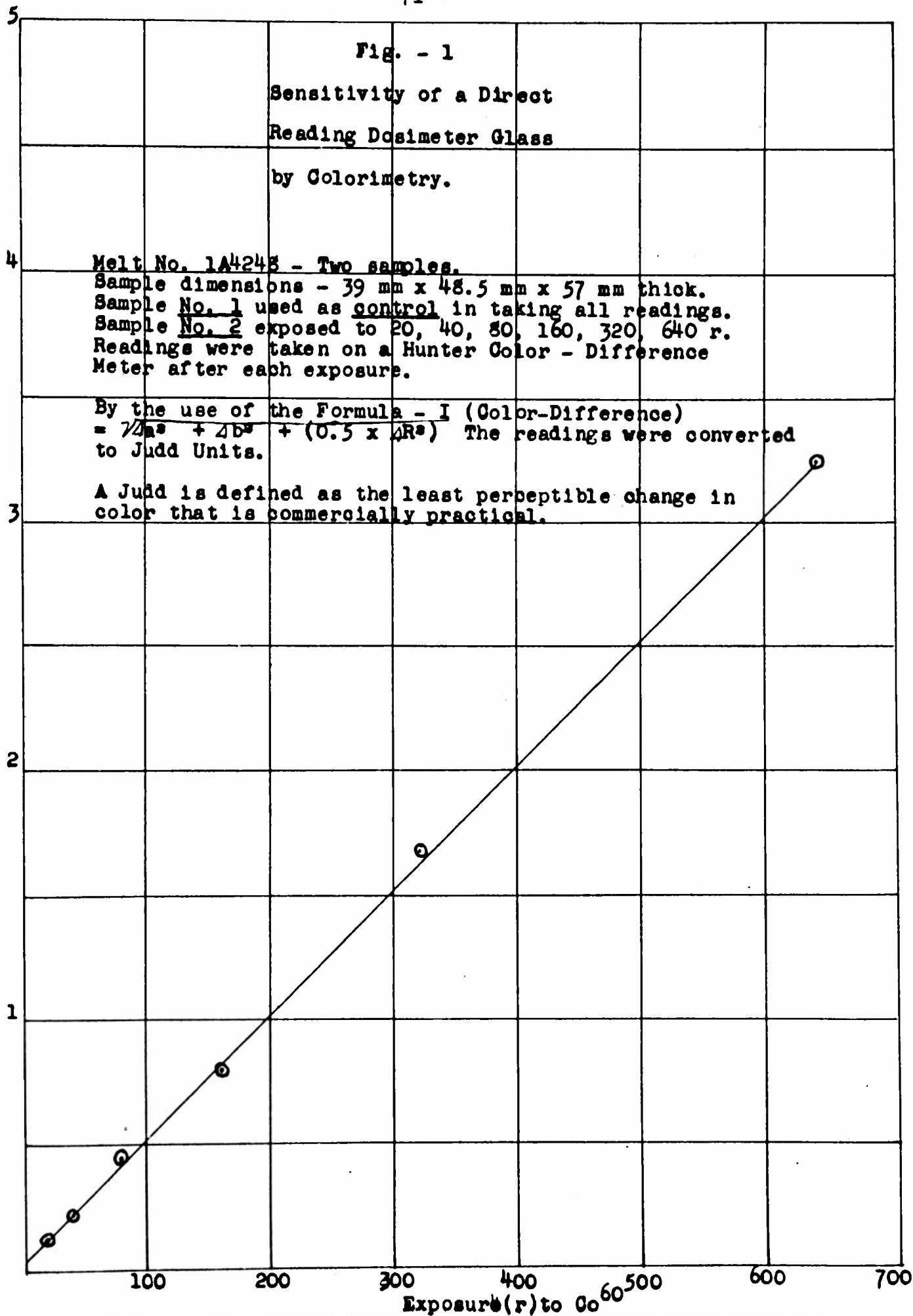
APPENDIX XI  
(Continued)

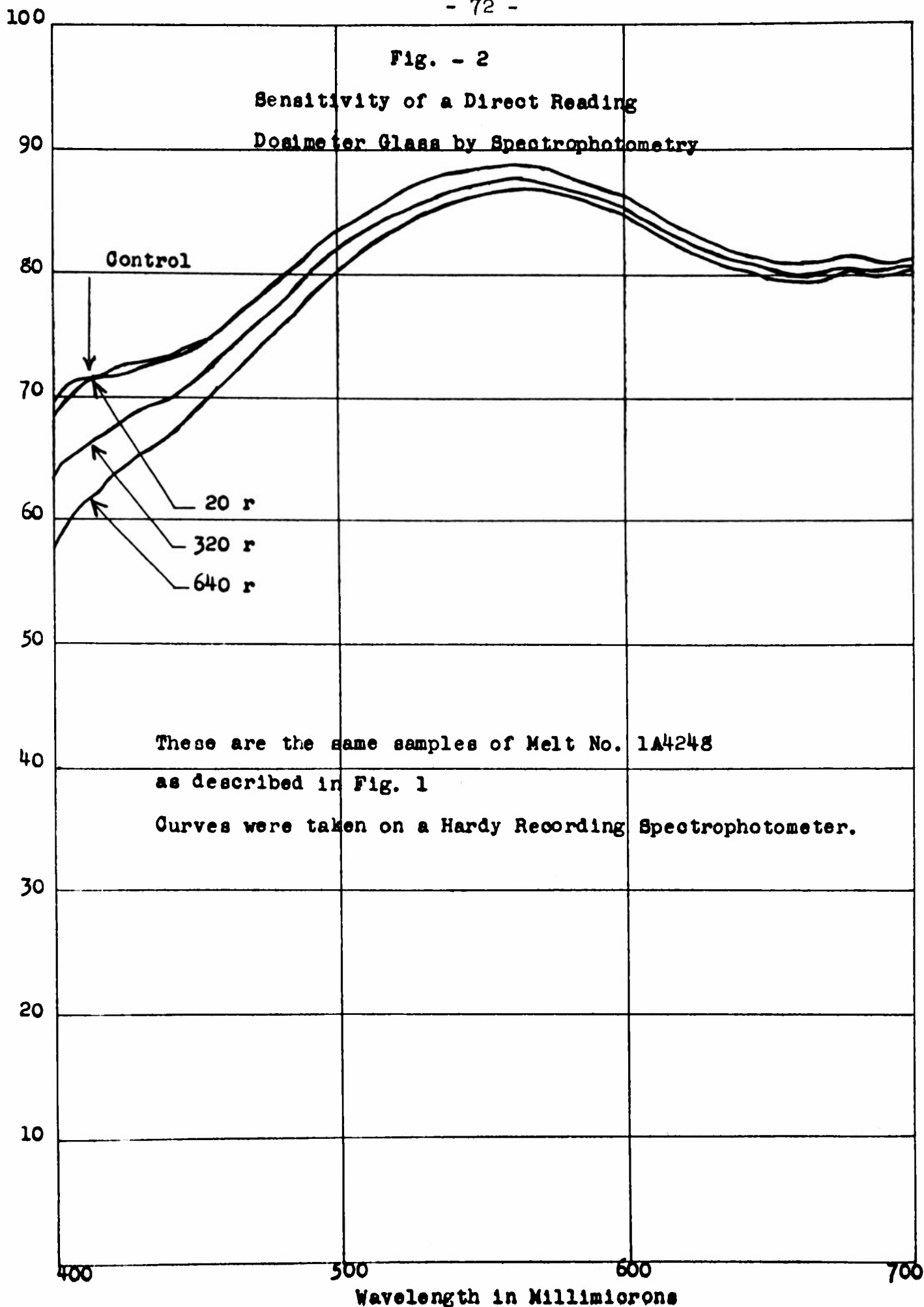
<u>Composition - Wt.%</u>	<u>Exposure (r)</u>	<u>Visual Evaluation Through 1" Thickness</u>
Al(PO <sub>3</sub> ) <sub>3</sub> - 85 S - 15	2000	0
Ca(PO <sub>3</sub> ) <sub>2</sub> - 85 S - 15	2000	0
Ba(PO <sub>3</sub> ) <sub>2</sub> - 85 S - 15	2000	0
Al(PO <sub>3</sub> ) <sub>3</sub> - 40 KPO <sub>3</sub> - 20 Ba(PO <sub>3</sub> ) <sub>2</sub> - 20 S - 20	2000	0
Al(PO <sub>3</sub> ) <sub>3</sub> - 70 KF - 20 S - 10	500	0

NOTE: The glasses made in this field were of experimental size, 50 - 100 cc melts, and were made in zircon crucibles where possible.



Color Difference in Judd Units





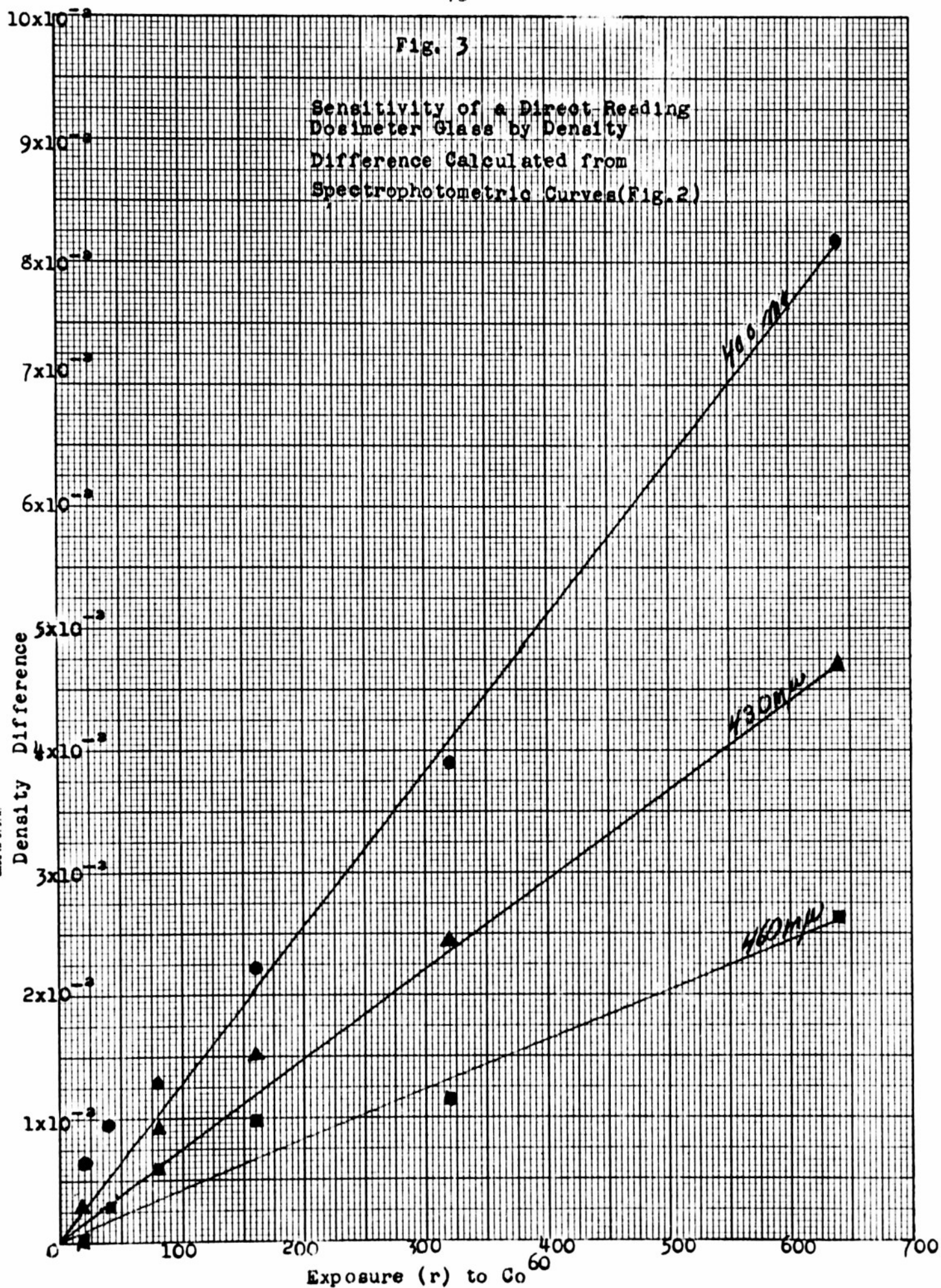




Fig. - 4

Exposure Temperature Effect  
(See Appendix V, pg. 2)

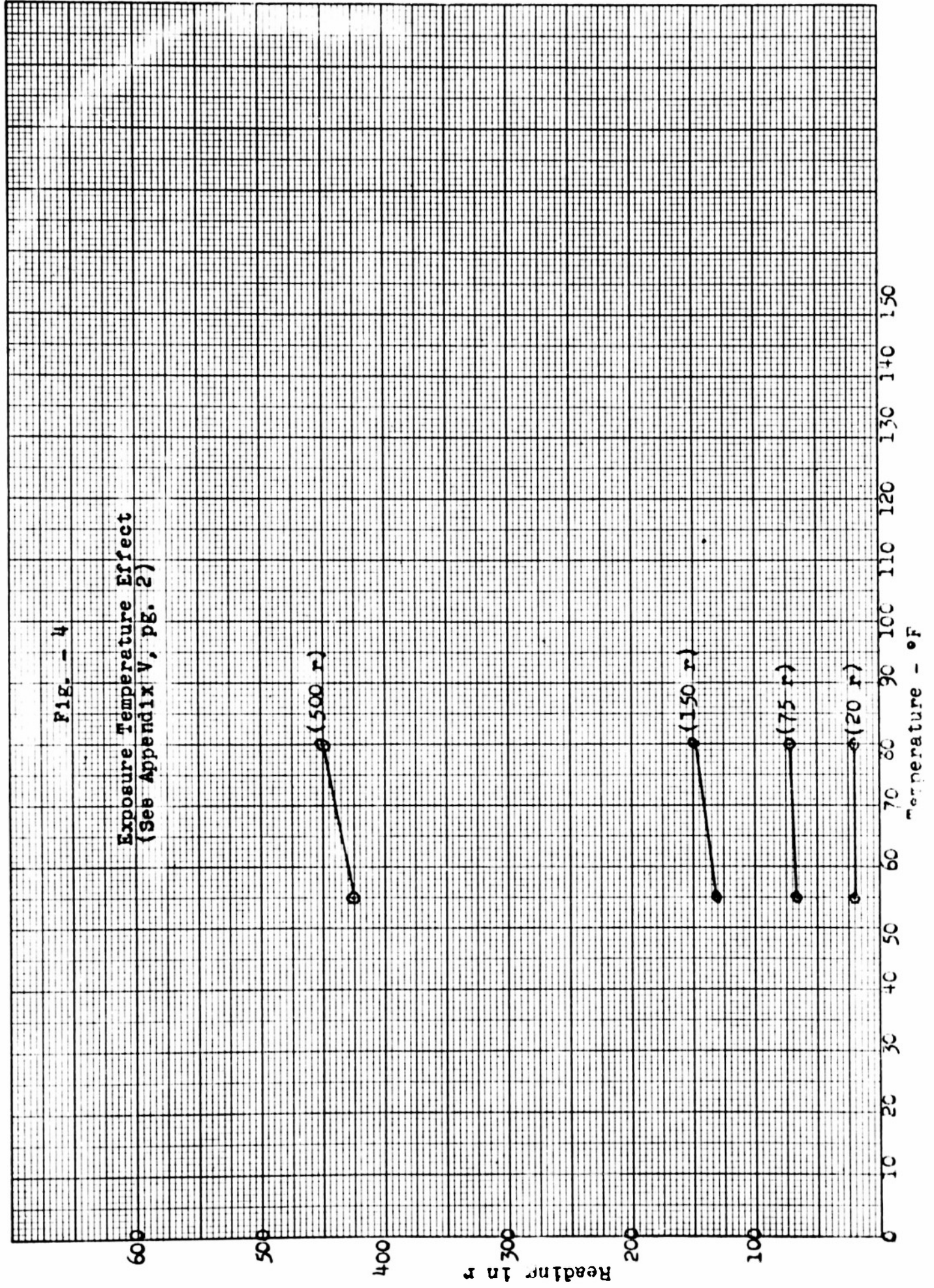
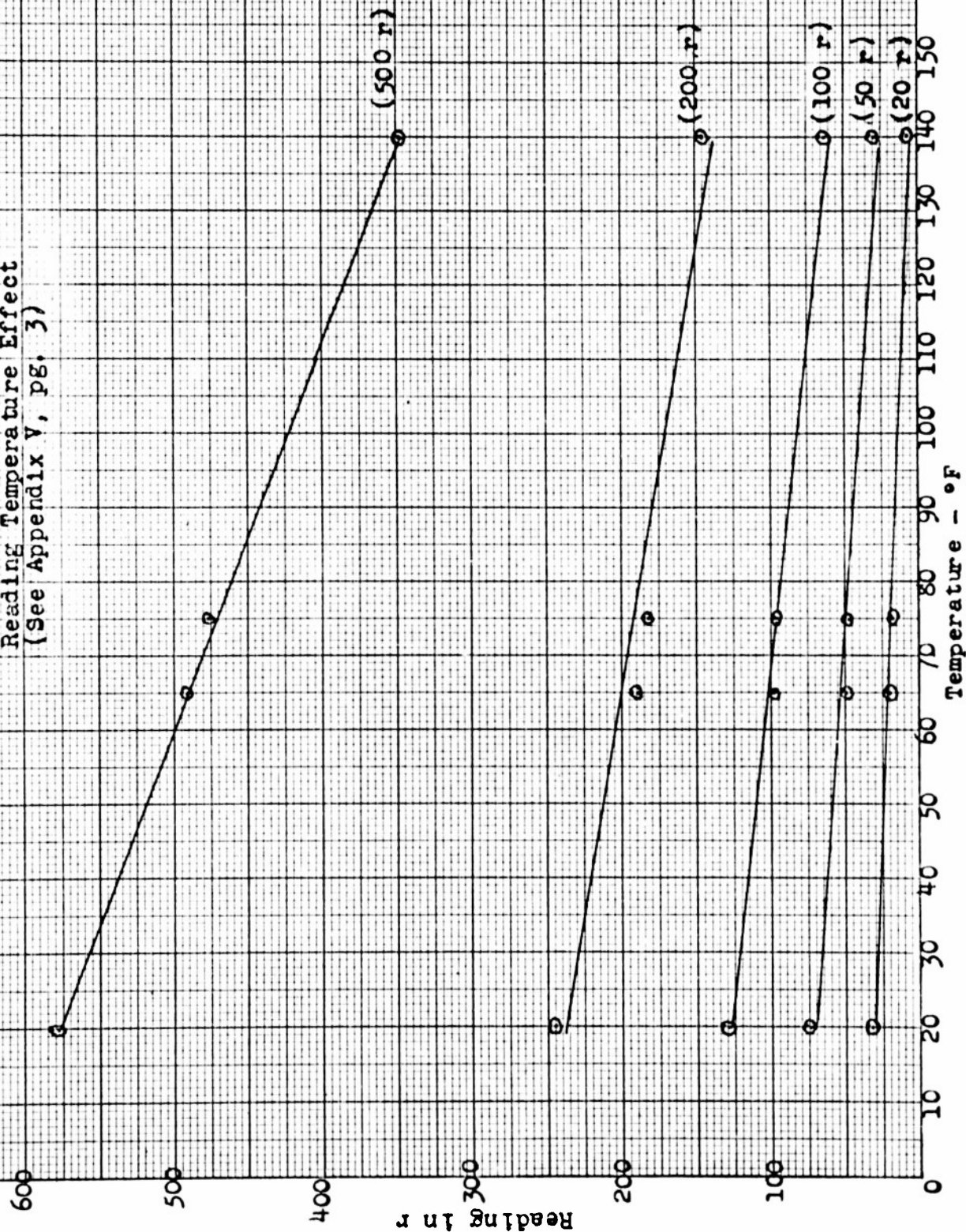


Fig. -5  
Reading Temperature Effect  
(See Appendix V, pg. 3)



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